IMPERIAL MYCOLOGICAL INSTITUTE
5 NOV. 1940

THE

SCIENTIFIC PROCEEDINGS

OF THE

ROYAL DUBLIN SOCIETY

Vol. 22, N.S., Nos. 25–32. SEPTEMBER, 1940.

25.—ATMOSPHERIC POLLUTION IN DUBLIN DURING THE YEAR 1939. By A. G. G. Leonard, Bridget P. McVerry, and D. Crowley.

26.—STUDIES IN PEAT. Part 8. PRELIMINARY NOTE ON IRISH PEAT WAX (MONA WAX). By J. Reilly and J. A. Emlyn.

27.—REPORT OF THE IRISH RADIUM COMMITTEE FOR THE YEAR 1939. Including Reports from Oswald J. Murphy, M.B., B.Ch., St. Vincent's Hospital, Dublin; Oliver Chance, M.B., B.Ch., D.M.R.E., Richmond, Sir Patrick Dun's, Dr. Steevens', Rotunda, and Coombe Hospitals; Dr. R. E. Tottenham, City and County Hospital, Londonderry; and by St. Anne's Hospital, Dublin (*Radiologist*—Dr. Oliver Chance).

28.—THE PRODUCTION OF SANTONIN FROM IRISH-GROWN ARTEMESIA. By Peter J. Drumm, Ph.D., D.Sc., and William F. O'Connor, M.Sc.

29.—A MOLECULAR CONSTANT FOR SOURED MILKS. II. EFFECT OF PRESERVATIVES. By J. J. Ryan and G. T. Pyne (Department of Dairy Chemistry, University College, Cork).

30.—AWARD OF THE BOYLE MEDAL TO PROFESSOR JOSEPH REILLY.

31.—SALMON OF THE BALLISODARE RIVER. I.—HISTORY OF THE BALLISODARE FISHERY. By Arthur E. J. Went, Department of Agriculture, Fisheries Branch, Dublin. (Plate No. 7.)

32.—SOIL AND FRESH-WATER IODINE-CONTENT IN IRELAND IN RELATION TO ENDEMIC GOITRE INCIDENCE. By James C. Shee, Chemistry Department, University College, Cork. [Communicated by Professor J. Reilly.]

[*Authors alone are responsible for all opinions expressed in their Communications.*]

DUBLIN:

PUBLISHED BY THE ROYAL DUBLIN SOCIETY,
BALLSBRIDGE, DUBLIN.

HODGES, FIGGIS, AND CO.,
20 NASSAU STREET, DUBLIN.

WILLIAMS AND NORGATE,
36 GREAT RUSSELL STREET, LONDON, W.C. 1.

1940.

Price Six Shillings.

Royal Dublin Society.

FOUNDED, A.D. 1731. INCORPORATED, A.D. 1750.

The Scientific Meetings of the Society are usually held at 4.15 p.m. on the fourth Tuesday of every month of the Session (November to June).

The attention of authors is directed to the following extracts from the regulations governing the presentation of communications at Scientific Meetings of the Society, and the publication of papers in the Scientific or Economic Proceedings :—

> "An author who desires to present a communication at a Scientific Meeting of the Society shall furnish to the Registrar a fortnight previous to that meeting the title and an abstract (not exceeding 200 words) of his communication, together with an estimate of the time required for presentation.
>
> "An author who desires to have a communication published forthwith as a paper in the Proceedings of the Society shall furnish to the Registrar the full text and necessary illustrations at least a week before the meeting of the Committee of Science at which he desires publication to be considered. Meetings of the Committee of Science are usually held on the second Tuesday of each month from November to June inclusive.
>
> "A paper may be published either in the Scientific Proceedings or the Economic Proceedings of the Royal Dublin Society, as directed by the Committee of Science. The copyright of papers so published shall be the property of the Society.
>
> "Fifty copies of each paper shall be supplied free of cost to the Author or Authors.
>
> "Additional copies may be obtained at Cost Price if applied for by the Author when returning the proofs."

Authors are requested to apply to the Registrar for further information concerning the preparation of papers and illustrations for press.

Authors of biological papers involving extensive numerical observations, are requested to consult the recommendations of the British Association Committee on Biological Measurements, 1927, obtainable from the British Association, Burlington House, W. 1, price 6d. Arrangements have been made whereby original data, too extensive for complete publication, may be deposited at the British Museum (Natural History), or with the Royal Society of Edinburgh, and so be made available for future workers. Authors desirous of depositing data, whether zoological or botanical, in this manner, should communicate with either the Keeper of Zoology, Natural History Museum, S.W. 7, or the General Secretary, The Royal Society of Edinburgh, 22 George Street, Edinburgh, enclosing full bibliographic reference to the publication in which the results are summarised.

ERRATA.

Page 295. Last line. *For* "16 to 18 inclusive" *read* "16 and 17."
Page 296. 5th line. *For* "15 and 16" *read* "16 and 17."

No. 25.

ATMOSPHERIC POLLUTION IN DUBLIN DURING THE YEAR 1939.

By A. G. G. LEONARD, BRIDGET P. McVERRY,

AND

D. CROWLEY.

[Read March 19. Published separately May 16, 1940.]

The work recorded in this paper is a continuation of that by Leonard and McVerry (Sci. Proc. R.D.S., 1939), but a second gauge and apparatus for measuring sulphur dioxide have been operated at the Albert Farm, Glasnevin, so that comparative results have been obtained.

Results obtained with standard gauges.

Detailed figures are given for Leinster Lawn and Albert Farm in Tables 1 and 2 respectively. Owing to interference with the gauge at the Farm no results were obtained for the month of April.

Fig. 1 gives a comparison of soluble solids at the two stations, from which it may be seen that the graph for the Albert Farm follows that for Leinster Lawn fairly closely, but at a lower level. Soluble solids at Leinster Lawn were deposited at the rate of 67 tons per sq. mile, and (excluding April) were about 1·6 times those deposited at the Albert Farm.

Fig. 1 also gives the graphs for insoluble solids. There is little in common between the graphs, the solids due to the city atmosphere exerting a preponderating influence.

Insoluble solids at Leinster Lawn were deposited at the rate of 106 tons per sq. mile, and (excluding April) were about 4·4 times those at the Albert Farm.

pH values of rain water.

The pH values of the waters collected show a general tendency to decrease in the winter months, and the values obtaining at the Albert Farm are on the whole slightly higher than those at Leinster Lawn.

Suspended Impurity as found with the Automatic Filter.

Fig. 2 gives a graph of mean monthly shade values for the years 1938 and 1939 at University College, Merrion Street, and shows very clearly the seasonal variation, the winter months showing a much higher degree of pollution than the summer months, when coal consumption is at a minimum.

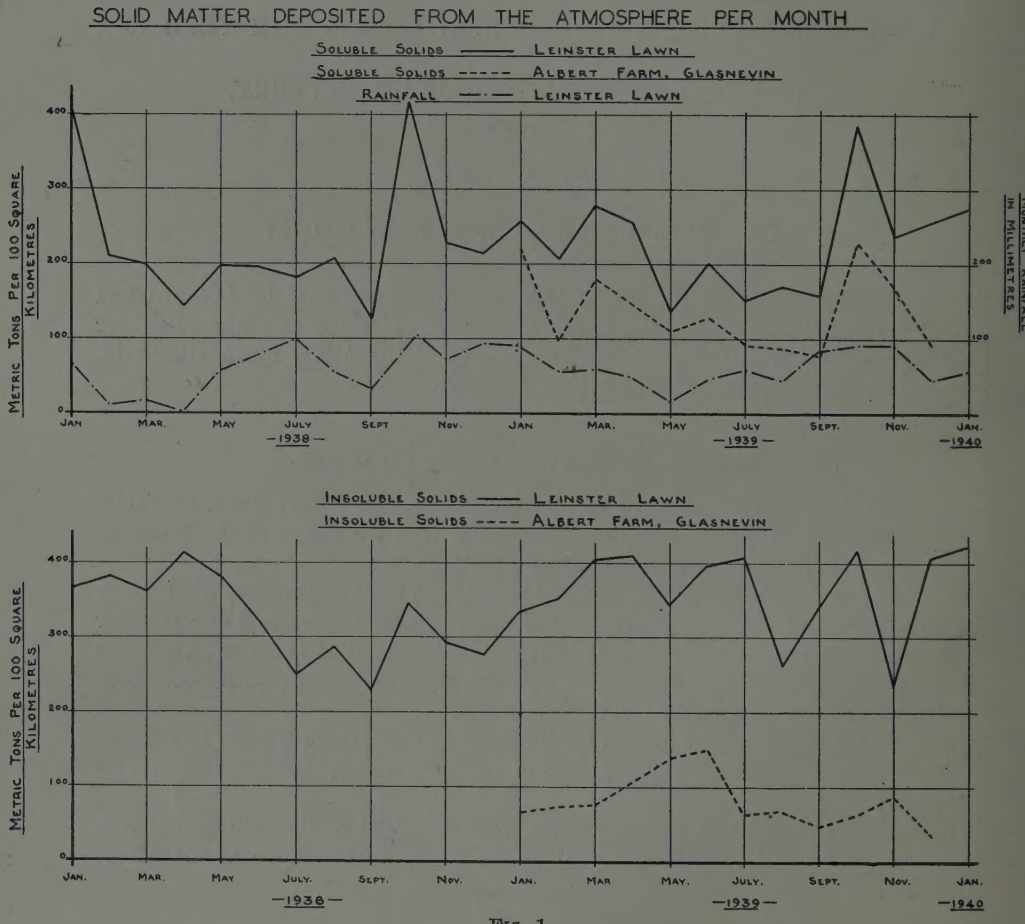


Fig. 1.

Pollution by Sulphur Dioxide.

Fig. 2 shows a close similarity between the graphs for mean monthly shade due to suspended impurity, and monthly measurement of sulphur dioxide

(plotted as SO_3) absorbed by lead peroxide during the years 1938 and 1939 at Leinster Lawn.

When the values for SO_3 and mean monthly shade were plotted as in Fig. 3, the points lay fairly uniformly about a straight line. As both these quantities are due to the combustion of coal, such a result might be expected in a city where most of the pollution is due to domestic coal fires.

The equation of the straight line graphed in Fig. 3 is $M = 0{\cdot}63\ S - 0{\cdot}17$, where M = mean monthly shade and S = milligrams SO_3 per 100 cm.^{2} per day. Fig. 2 gives a graph for sulphur dioxide measured monthly at the Albert Farm during 1939; it follows the trend of the corresponding graph for Leinster

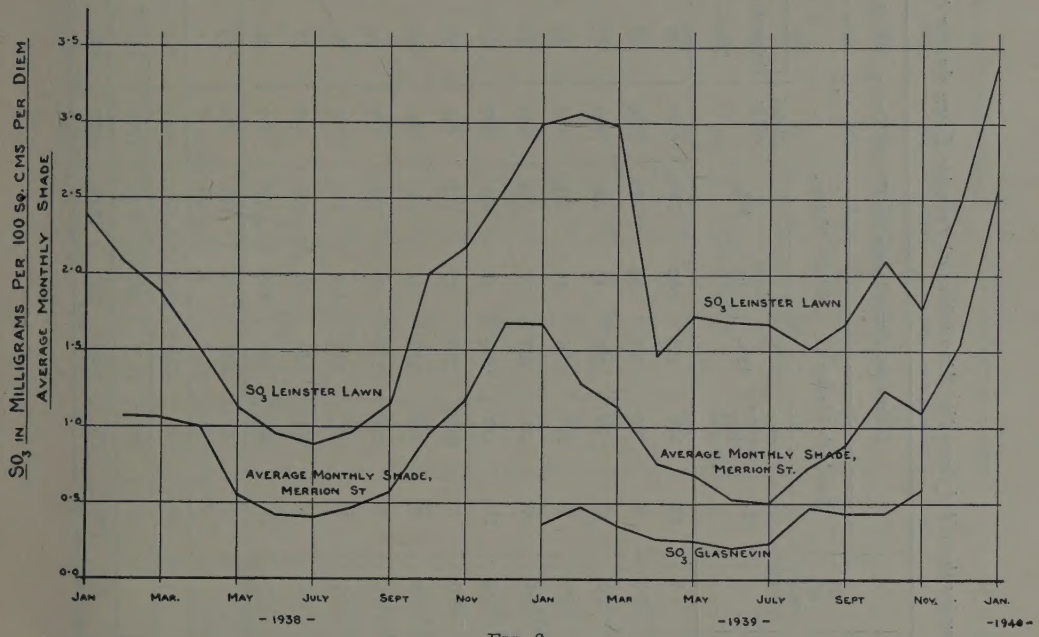


FIG. 2.

Lawn at a lower level, the sulphur dioxide recorded at Leinster Lawn in 1939 being about 5·4 times that at the Farm.

Applying the equation above mentioned to the peak figure of 0·59 mg. for SO_3 at the Farm, which occurred in November, 1939, one derives an average monthly shade of 0·2, which is about one-fifth of the figure obtained with the automatic filter at Leinster Lawn for the same month, and one-half of the lowest figure recorded there for any month in the period 1938–9.

MEASUREMENT OF DAYLIGHT.

The following quotation is taken from the 14th Report of the Atmospheric Pollution Research Committee for the year ended March 31, 1928:—

TABLE 1.—*Impurity deposited from the Atmosphere at Leinster Lawn during the year 1939.*

	Rainfall. mm.	pH of rainwater.	Grams per square Decametre (Metric Tons per Hundred Square Kilometres).									
			Insoluble Matter.			Soluble Matter.		Total solids.	Included in Soluble Matter.			
			Tar.	Carbonaceous other than tar.	Ash.	Loss on ignition.	Ash.		Sulphates. (SO_3).	Chlorine. (Cl).	Ammonia. (NH_3).	Lime. (CaO)
January	90	4·7	13	100	222	102	155	592	47	72	6	34
February	57	5·5	9	92	251	60	147	560	53	41	4	34
March	60	5·5	12	123	269	48	230	682	72	57	3	51
April	48	5·7	7	128	275	81	175	665	60	38	2	58
May	17	6·4	7	128	207	17	119	481	40	13	–	30
June	46	6·4	11	136	250	70	132	599	43	26	1	34
July	59	6·0	8	133	168	33	119	461	38	24	1	26
August	45	4·8	9	96	156	31	139	431	52	18	2	29
September	85	5·1	7	135	200	28	130	500	48	17	–	28
October	92	4·7	7	160	248	119	224	803	86	115	5	48
November	91	4·6	6	94	144	65	174	483	61	68	2	25
December	46	4·7	13	150	243	103	150	659	63	34	4	42
Mean Monthly	61		9 B	123 B	219 B	63 A	158 B	576 B	55 A	44 B	2 A	37
Summer Total	300		49	756	1256	260	814	3137	281	136	6	205
Winter Total	436		60	719	1377	497	1080	3779	382	387	24	234
Annual Total	736		109	1475	2633	757	1894	6916	663	523	30	439

TABLE 2.—*Impurity deposited from the Atmosphere at Glasnevin during the year 1939.*

	Rainfall.	pH of water.	Grams per square Decametre (Metric Tons per Hundred Square Kilometres).								
			Insoluble Matter.			Soluble Matter.		Total solids.	Included in Soluble Matter.		
	mm.		Tar.	Carbonaceous other than tar.	Ash.	Loss on ignition.	Ash.		Sulphates. (SO_3)	Chlorine. (Cl).	Ammonia. (NH_3).
January	88	5·78	4	30	32	75	150	291	37	32	5
February	60	6·24	5	19	49	25	71	169	29	13	3
March	65	5·46	4	42	30	72	110	258	25	25	7
April	52	7·33	—	—	—	—	—	—	—	—	—
May	20	6·64	4	50	83	53	52	242	23	6	1
June‡	35	6·81	3	54	93	69	61	280	21	11	3
July	67	5·5	2	30	29	38	55	154	23	11	3
August	45	5·33	1	32	33	54	34	154	25	5	4
September	86	4·84	3	19	25	43	34	124	6	6	1
October	67	5·16	2	23	36	120	110	291	20	50	8
November	88	4·71	5	32	47	68	100	252	49	37	6
December	58	4·72	2	12	20	41	50	125	36	14	5
Mean Monthly	61		3 A	31 A	43 A	60 A	66 A	213 A	27 A	19 A	4 A
Summer Total	305		13*	185*	263*	257*	236*	954*	98*	39*	12*
Winter Total	426		22	158	214	401	591	1386	196	171	34
Annual Total	731		35†	343†	477†	658†	727†	2340†	294†	210†	46†

* Five months only. † Eleven months only. ‡ Position of gauge changed.

"During the years 1926 and 1927 a series of tests have been carried out at Salford with the idea of arriving at a comparative measure of the strength of sunlight in different districts. The method used is one which was adopted by the Manchester Air Analysis Committee, and it has been found to be simple in working and to give reasonably accurate results.

"The test consists in the exposure of a solution of potassium iodide acidified with sulphuric acid in a 2 oz. glass bottle, in the presence of air. Free iodine is liberated by the action of the sunlight, and the amount found is proportional to the light received. The glass bottle transmits very little of the ultra-violet,

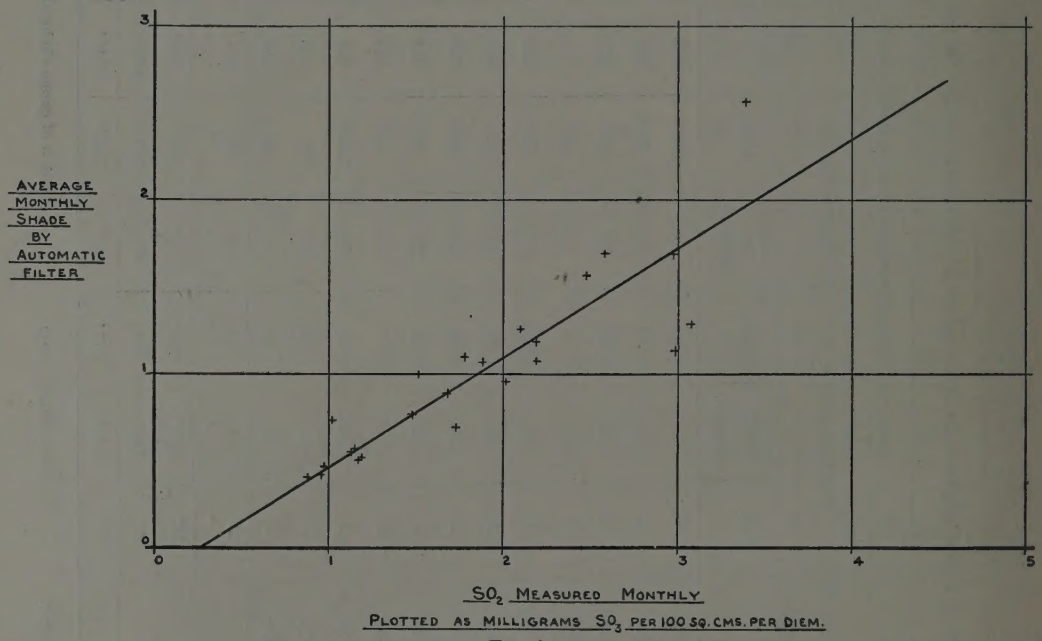


FIG. 3.

but sufficient photo-chemical action takes place to give comparative results for the strength of light received in different districts.

"The solutions used are as follows:—

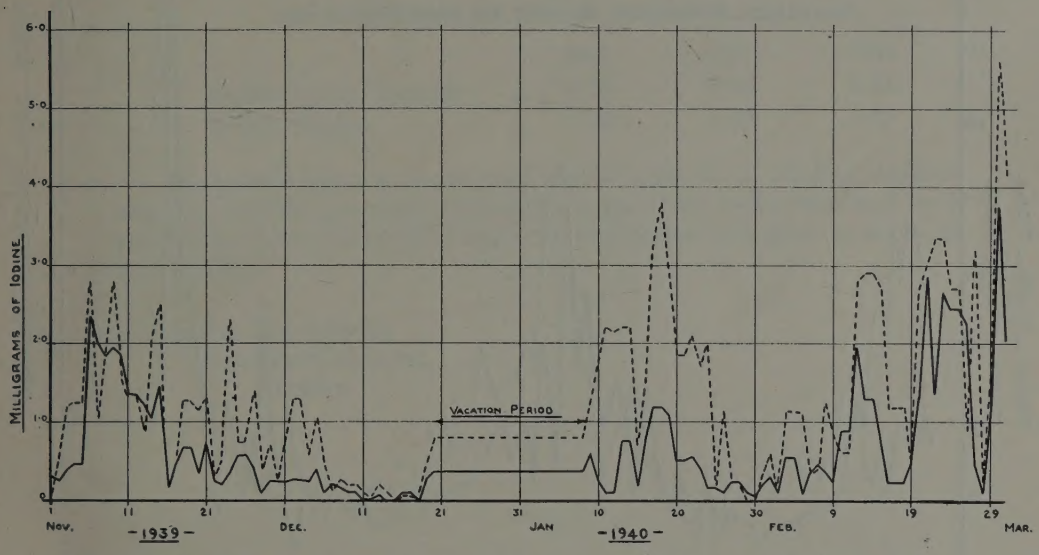
"Potassium iodide solution, 2 per cent.; sulphuric acid solution, 11·85 g. per litre; 10 c.c. of each of these solutions are placed in the glass bottle. After exposure the free iodine is titrated against standard thiosulphate solution, 1 c.c. = 0·001 g. I. A fresh bottle is exposed each morning, and the bottle exposed the previous day is placed in a closed tin until titrated. Each bottle is placed on a white tile during exposure, in such a position that no shadow falls on it."

Fig. 4 shows the measurement of daylight, expressed as milligrams of iodine, for University College, Merrion Street, and for the Albert Farm, from November 1, 1939, to February 29, 1940. During the College Christmas vacation one long exposure was made in each case. The graphs show that in general the daylight at Merrion Street is much less than at the Farm.

A summary of the measurements is given in the following table:—

Milligrams of Iodine Liberated.

	Nov.	Dec. 1–19.	Dec. 20–Jan. 9.	Jan. 9–31.	Feb.
U.C.D., Merrion St. ...	23·2	2·65	7·8	10·2	28·6
Albert Farm ...	35·4	7·15	16·0	33·4	47·1
% Loss at Merrion St. ...	34·5	63	51	70	39



COMPARISON OF SUNLIGHT AS MEASURED BY LIBERATION OF IODINE FROM POTASSIUM IODIDE

—— UNIVERSITY COLLEGE, MERRION STREET.
----- ALBERT FARM, GLASNEVIN.

FIG. 4.

The total loss of daylight at Merrion Street from November 1, 1939, to February 29, 1940, was 45 per cent. of the daylight received at the Albert Farm.

The authors wish to express their thanks to Mr. T. Breaden, who prepared all the solutions used in the above measurements, and carried out the daily determinations at Merrion Street.

POLLUTION BY SUSPENDED MATTER AND DEATHS FROM RESPIRATORY DISEASES.

It is a well-established fact that the death-rate from respiratory diseases is higher in cities than in rural areas, and in large cities, such as Manchester, periods of fog are followed by a rise in the death-rate from such diseases. City fogs are due to an increase in the amount of suspended matter present in the air. A day upon which at any hour a shade number of 4 or more is recorded by the automatic filter is classed as a "hazy" day. It frequently

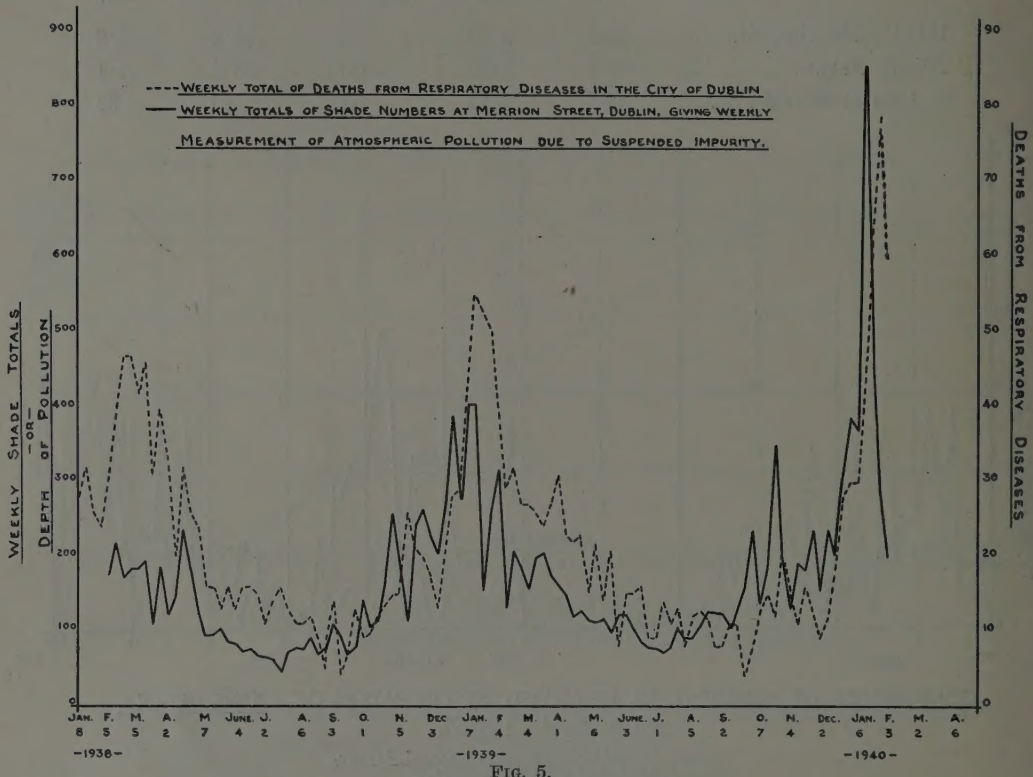

----WEEKLY TOTAL OF DEATHS FROM RESPIRATORY DISEASES IN THE CITY OF DUBLIN
—— WEEKLY TOTALS OF SHADE NUMBERS AT MERRION STREET, DUBLIN, GIVING WEEKLY MEASUREMENT OF ATMOSPHERIC POLLUTION DUE TO SUSPENDED IMPURITY.
WEEKLY SHADE TOTALS -OR- DEPTH OF POLLUTION
DEATHS FROM RESPIRATORY DISEASES
900
800
700
600
500
400
300
200
100
0
90
80
70
60
50
40
30
20
10
0
JAN. 8 F. 5 M. 5 A. 2 M 7 JUNE. 4 J. 2 A. 6 S. 3 O. 1 N. 5 DEC 3 JAN. 7 F 4 M 4 A. 1 M. 6 JUNE. 3 J. 1 A. 5 S. 2 O. 7 N. 4 DEC. 2 JAN. 6 F. 3 M. 2 A. 6
-1938-
-1939-
-1940-

FIG. 5.

happens, however, that the shade totals for certain "ordinary" days exceed those for certain hazy days when the haze did not persist. In other words, the actual total of pollution by suspended matter on clear or ordinary days may exceed that on certain hazy days. Instead of confining our attention to hazy days, we have summed the shade numbers recorded at Merrion Street for all days in each week of 1938, 1939, and part of 1940, thus obtaining a graph (Fig. 5) representing the depth of pollution in each week.

When compared with the weekly total of deaths from respiratory diseases in Dublin County Borough the similarity of the curves during the winter months is striking.

In general, it may be said that any pronounced rise in pollution during the winter is followed shortly by a rise in the death-rate.

It is to be remembered that high pollution by suspended impurity is accompanied by corresponding high pollution by sulphur dioxide, and also that periods of high pollution by these two quantities are always periods of low temperature.

The temperature factor, however, is more or less common to the whole county, and it is significant to compare the death-rate from respiratory diseases in Dublin County Borough with that in the rest of the county.

Death-rate per 1,000 of population.

	1936.	1937.	1938.
Dublin County Borough ...	2·92	2·88	2·32
Dublin County	1·85	1·87	1·50

The authors desire to express their thanks to Mr. M. G. Dowling, Assistant Registrar-General, who supplied them with copies of the weekly returns of births and deaths, and to University College for continuation of a grant in aid of the investigation.

CHEMICAL DEPARTMENT,
UNIVERSITY COLLEGE,
DUBLIN.

No. 26.

STUDIES IN PEAT.

Part 8.

PRELIMINARY NOTE ON IRISH PEAT WAX (MONA WAX).

By J. REILLY and J. A. EMLYN.

[Read April 23. Published May 16, 1940.]

In an earlier communication (1) the effect of solvents upon yield of extract from peat has been described, and analytical data given. Mixtures of solvents were shown to give larger yields of extract in general than single solvents. Also, the behaviour of azeotropic mixtures on distillation in presence of water has been discussed (2), this being important when extraction of air-dried peat containing up to 30 per cent. water is attempted with mixed solvents.

Industrially, choice of solvent is limited by costs to three or four, and before final choice is made it becomes necessary to consider the effect of solvent upon the type of extract produced, for the nature of the product determines its ultimate value.

Briefly, the constituents of peat extractable by organic solvents may consist of resins, bituminous matter, and wax. Wax here refers to esters of higher fatty acids and alcohols, together with the free acids and alcohols of the same order, and possibly hydrocarbons and sterols if present. It is suggested that wax of this type derived from Irish peat might be called Mona Wax.

Solvents are selective to a large extent, and it should be possible therefore, by use of the correct solvent or mixture of solvents, to obtain the above three constituents separately, or as a mixed extract of two in varying proportions, or as a "total extract" of three.

The conception of polar and non-polar molecules applied to solvents has thrown considerable light on their selectivity. Jordan (3) has reviewed very clearly modern ideas of the mechanism of solution, showing how the orientation of the surface molecules of a solvent affects its power of miscibility with other substances of like orientation. As a general rule it is found that substances of a non-polar or weakly polar nature, e.g. paraffins, fats, waxes, bitumen, rubber, and certain resins, are readily dissolved by the non-polar group of solvents, viz. paraffin and benzene hydrocarbons. Strongly polar solvents, e.g. lower alcohols, are excellent for dissolving many resins, dyestuffs, etc., but are poor for non-polar materials such as those listed above.

As an example, a sample of peat which gave 8·4 per cent. crude wax with petroleum spirit, on extraction with a mixture of the same petroleum with isopropyl alcohol (70 : 30) yielded 10·6 per cent. extract. Of this 10·6 per cent., 2·0 per cent. was readily extracted by cold ethyl alcohol (to give mainly

resinous matter with possibly small amounts of low-melting free acids and esters present in the wax), leaving 8·6 per cent. residual extract similar to the crude wax obtained by petroleum alone.

Typical analyses of the two products obtained with petroleum and petroleum/alcohol mixtures are given below:—

	Petroleum Extract.	Petroleum/Alcohol Extract.
S.G. at 20° C.	1·01	1·03
Softening Point	65° C.	68° C.
Melting Point	69° C.	69–73° C.
Acid Value	35	42
Saponification Value	93	126
Ester Value	58	84
Iodine Value	34	37

The analytical figures give little indication of the considerable physical differences between the two extracts, differences which are all-important to users of waxes.

The petroleum/alcohol extract softens over a longer range and remains more viscous when melted. It is not completely soluble in such solvents as white spirit and lower boiling hydrocarbons, the solubility varying according to the percentage of resinous matter in the peat. When solid, it breaks with a smooth, shiny fracture resembling that of rosin or pitch, and shows none of the crystal structure which appears in the crude wax obtained by petroleum spirit alone.

The resinous matter soluble in cold ethyl alcohol when isolated from the petrol/alcohol extract is clear, red-brown in colour, and slightly soft and tacky when cold. It has no definite melting point, but softens gradually over a long range of temperature, remaining viscous at temperatures well above 100° C.

It is mainly acidic. Following the scheme of Tschirch (4) it may be divided into the following fractions[1]:—

Acids Extracted with 1% $(NH_4)_2CO_3$.	Acids Extracted with 1% Na_2CO_3.	Acids Extracted with 0·1% KOH.	Acids Extracted with 1% KOH.	Residue.
22%	28·5%	10%	12%	27·5%

All these fractions are resinous in appearance, and very resistant to further purification.

Many samples of Irish peat have been extracted selectively in this way. Yields vary according to the locality and quality of the peat, but in general it is found that extraction with the solvents mentioned gives three to four times as much crude wax as alcohol-soluble resin. Yields for good quality peat (anhydrous) are of the order:—

Crude Wax ...	8%–10%
Resinous Matter ...	3%–4%

[1] Reilly and Atkins—unpublished work, U.C.C.

Contrary to expectation, in the extraction of peat with petroleum hydrocarbons the presence of moisture in the peat does not appear to hinder efficient removal of wax. Samples containing up to 45 per cent. moisture have been readily extracted.

Clayton (5) points out that Schlaepfer found finely-divided carbon enabled 70 per cent. by volume of water to be dispersed in 30 per cent. Kerosene to give a very stable emulsion (6). It was found impossible to make an oil-in-water emulsion with carbon. Other workers have confirmed this, and also found that silica gave just the reverse effect, forming oil-in-water emulsions.

It is probable that emulsions of water-in-oil type tend to form in presence of the finely divided carbonaceous matter in the ground peat. Consequently the water is not able to act as a protective film preventing solvent coming in contact with the wax. Also, peat wax itself when melted forms very stable emulsions with water of the water-in-oil type.

The crude wax obtained either by extraction of peat with petroleum or after removal of cold alcohol-soluble resinous matter from a mixed extract, is still very impure and dark brown in colour. It may contain bituminous matter in considerable amounts, also certain resins of the non-polar type (7), i.e. those soluble in petroleum or benzene hydrocarbons but relatively insoluble in alcohols.

The selective nature of different solvents is not sufficiently marked to give a simple separation of these impurities, since wax and impurities are of the same group of non- or weakly polar materials. Many extractions and fractional crystallisations are required gradually to concentrate wax relatively free from undesirable matter.

Repeated extraction with boiling ethyl alcohol removes approximately 54 per cent. of the crude wax. On cooling the alcohol solution, a light brown wax is precipitated and separated by filtration. The clear filtrate after removal of solvent leaves a soft, gummy residue of low-melting resinous material, varying in amount from 5 per cent.–20 per cent. of the original crude wax, if this has been obtained by petroleum extraction.

The residue insoluble in alcohol, containing almost all the black, bituminous impurities, resembles pitch in appearance but melts to a mobile liquid.

	Wax Soluble in hot Ethyl Alcohol.	Residue Insoluble in Ethyl Alcohol.
Melting Point	74° C.	66° C.
Acid Value	43	Nil
Saponification Value ...	116	91
Ester Value	73	91
Iodine Value	24	28

It is of interest to compare mona wax with the other wax obtained from fossilised plant remains, viz. German montan wax from lignite. Crude montan wax is well known as a hard, dark brown wax widely used in many industries. A typical analysis is given below:—

Crude Montan Wax (Riebeck).

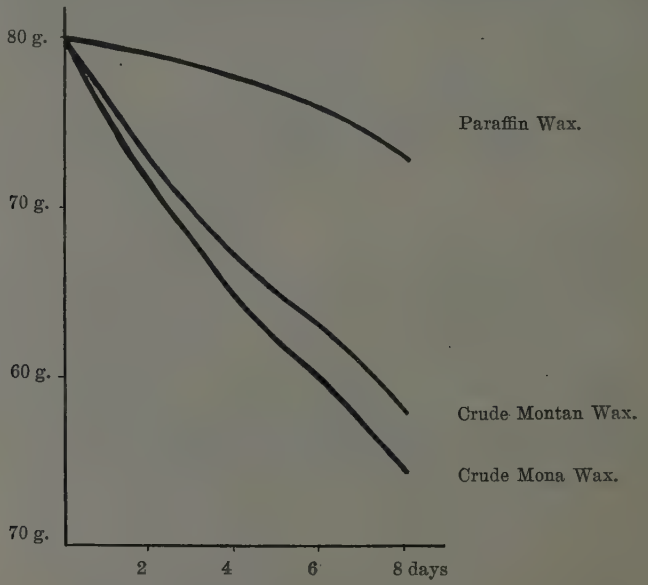
Softening Point	81° C.
Melting Point	83° C.
Acid Value	30
Saponification Value	66
Ester Value	36
Ash	0·3%

Crude mona wax is softer in texture than montan wax and has a melting point 10°–15° C. lower. In other physical properties they show some resemblance. Both are characteristic in assisting formation of emulsions of the water-in-oil type: the S.G. is higher than for most natural waxes (1·00–1·01 at 15° C.): the dielectric coefficients are of the same order. Values for mona and montan waxes, also a comparison with paraffin wax, have been determined by Dr. R. G. Allen, of University College, Dublin, and are given in the following table:—

Dielectric.	Permittivity or Specific Inductive Capacity.	Power Factor. (Cos θ.)	Specific Insulation Resistance. (Ohms per cm. cube.)	Dielectric Strength. (Volts r.m.s. per cm.)
Crude Mona Wax ...	2·85	·0215	$5{\cdot}95 \times 10^{11}$	342,000
Montan Wax	2·6	·0157	$8{\cdot}9 \times 10^{11}$	288,000
Refined Paraffin Wax M.p. 55° C.	2·13	·0063	$2\ 72 \times 10^{12}$	117,000

Testing Voltage ... ... 6,000 r.m.s.
Frequency ... ... 50 cycles per sec.
Temperature ... ... 12–15° C.

Solvent retention power, another important factor commercially, e.g. in polish manufacture, may be illustrated by the graph, showing loss in weight of a wax/white spirit mixture on exposure to air. Here again, values are of the same order.



Wax Mixture: 25 g. wax.
55 g. solvent.

The melting point of mona wax may be raised to that of montan wax by treatment with lime, forming calcium soaps of part of the free acids present, but in spite of higher m.p. the treated wax remains softer than montan in texture, indicating that the lower melting constituents may be mainly in the unsaponifiable portion of the wax. The unsaponifiable matter of the crude wax (over 50 per cent.) is readily divided into constituents soluble and insoluble in light petroleum (range 40°–60° C.). The former (40 per cent. of total unsaponifiable matter) is dark brown in colour, m.p. 57°–59° C., and breaks with a characteristic fracture showing a finely fibrous surface.

The residue insoluble in light petroleum (60 per cent. of unsaponifiable matter) is lighter in colour, with no definite melting point. It is very viscous at 100° C., and when cold has a resinous appearance with smooth fracture.

Investigation of the constituents of montan wax has been undertaken by several workers, and reported from time to time. Pschorr, Pfaff, and Berndt (8) give the composition of the crude wax as :—

30 per cent. montan resin (soluble in alcohol).

17 per cent. free montanic acid, $C_{28}H_{56}O_2$.

28 per cent. esterified montanic acid.

25 per cent. alcohols (equal mixtures of $C_{26}H_{54}O$, $C_{30}H_{62}O$ and small amounts of tetracosanol, $C_{24}H_{50}O$).

Montanic acid, according to Halde, Bleyberg, and Vohrer (9), is n-octacoxinoic acid, m.p. 89° C. Tropsch and Kreutzer (10) have reported $C_{27}H_{54}O_2$, $C_{29}H_{58}O_2$.

Owing to the intense colour and nature of the impurities, methods of refining montan and mona waxes are necessarily drastic, involving high temperature distillation with superheated steam, or the use of strong oxidising agents, e.g. chromic acid. It is to be expected, therefore, that the refined waxes will be different in constitution from the crude material.

Thus Marcussen and Lederer (11) find distilled montan wax to be composed of :—

56 per cent. wax acids.

28·6 per cent. montanone, m.p. 59°–60° C.

13·4 per cent. unsaturated hydrocarbons (iodine value 59; m.p. 28°–32° C.).

A wax purified with chromic acid was found by them (12) to contain 76·2 per cent. wax acids insoluble in water

(mean molecular wt. 347; m.p. 75°–81° C.; Iodine value 1·8).

Roginskaya (13) has reported the presence of $C_{29}H_{58}O_2$, $C_{28}H_{56}O_2$, $C_{27}H_{54}O_2$ and an unidentified acid of lower molecular weight, in the alcohol-soluble wax from Russian peat, while Titow (14) gives a more complete analysis indicating—

1. 15 per cent.–20 per cent. hydrocarbons, viz. Tritriacontan $C_{33}H_{68}$ and Pentatriacontan $C_{35}H_{72}$.
2. Saponifiable portion consisting of $C_{25}H_{50}O_2$, carboceric acid, and an unknown oxyacid, esters of these acids and the alcohol $C_{27}H_{56}O$.
3. Resinous matter of cyclic acids and their esters with cyclic (saturated and unsaturated) alcohols.

He concludes that the crude extract from Russian peat is essentially different from that obtained from German lignite.

Mona wax, although similar to montan wax in many properties, differs from it considerably in texture and m.p. Its composition as a whole may therefore be expected to show distinct differences from that of montan wax, although Ryan and Dillon (15) indicate that the acid constituents may be closely related.

More recently, X-ray analysis of the complex mixtures of acids and alcohols has been of great value in determining the constituents which are so closely related that chemical separation is extremely difficult if not impossible. In this way Chibnall *et al.* (16) conclude that the fatty acids and alcohols present in waxes are all of even number C. atoms, and show how previously reported odd-number acids have proved to be mixtures.

In order to investigate these differences between mona and montan waxes, and gain some idea of the relation between the two fossil waxes, the constituents of the lower-melting mona wax and resin, also the esters present in the crude wax, which are split up in refining processes, are being studied further.

SUMMARY.

The effect of petroleum hydrocarbons and alcohols upon type of extract obtained from Irish peat is outlined. Properties of crude wax and resinous matter are given, and the wax compared with montan wax. Further work is being done on the composition of the crude wax and resin constituents.

We are indebted to Dr. R. G. Allen, of University College, Dublin, for determining the dielectric coefficients, and to the Industrial Research Council for permission to publish this paper.

REFERENCES.

1. REILLY ET AL.—J.S.C.I., **56**, 231 T. (1937).
2. REILLY ET AL.—Sci. Proc. Roy. Dubl. Soc., **22**, 149, 181, 187 (1939).
3. JORDAN.—"Solvents" (Eng. Ed., London), 1937.
4. A. TSCHIRCH AND A. STOCK.—"Die Harze" (Berlin), 1933, vol. 1.
5. CLAYTON.—"Emulsions" (London), 1935, p. 108.
6. J. Chem. Soc., **113**, 522 (1918).
7. DRUMMOND.—India Rubber Journal, 1938, **125**, 101.
8. Z. angew. Chem., **34**, 324 (1921). Ber., **53**, 2147 (1920).
9. Brennstoff-Chem., **10**, 108 (1929); **11**, 146 (1930).
10. TROPSCH AND KREUTZER.—Brennstoff-Chem., **3**, 177, 193, 212 (1922).
11. Fettchem-Umschau, **38**, 253 (1931).
12. *Ibid.* See also Ger. Pat. 565310 (1932).
13. J. Applied Chem., U.S.S.R., **9**, 108 (1936).
14. TITOW.—Brennstoff-Chem., **13**, 266 (1932).
15. Sci. Proc. Roy. Dub. Soc., **12**, 202 (1909).
16. CHIBNALL ET AL.—Biochem. J., **28**, 2189 (1934).

No. 27.

REPORT OF THE IRISH RADIUM COMMITTEE FOR THE YEAR 1939.

[Read MAY 28. Published separately JUNE 12, 1940.]

THERE has been a considerable reduction in the demand for Radon tubes for therapeutic purposes, only 1,160 tubes containing 8,630 millicuries having been issued during the year, as compared with 1,582 tubes containing 11,202 mc. during 1938.

Mr. S. D. Daly was awarded the Radium Exhibition falling vacant during the year.

Returns received from the chief users record the treatment of the following cases with radon, or radium element, during 1939:—

MALIGNANT CASES.

Dr. Oswald Murphy, St. Vincent's Hospital, Dublin	94
Dr. Oliver Chance, Richmond, Sir Patrick Dun's, Dr. Steevens', Rotunda, and Coombe Hospitals, Dublin	9
Dr. R. E. Tottenham, City & County Hospital, Londonderry ...	4
Dr. d'Abreu, City & County Infirmary, Waterford	4
Dr. Bethel Solomons, Dr. Steevens' Hospital, Dublin ...	1
St. Anne's Hospital, Dublin	165
Coombe Hospital, Dublin	7
Total, ...	284

NON-MALIGNANT CASES.

Dr. Oswald Murphy	76
Dr. Oliver Chance	34
Dr. Bethel Solomons	5
St. Anne's Hospital, Dublin	9
National Maternity Hospital, Dublin	1
Total, ...	125

The returns show that for the cases of malignant disease first seen during 1939 the numbers treated by the different methods were as follows:—

No. of cases seen	889
„ „ treated	709
„ „ „ by Surgery alone	45
„ „ „ by Radium alone	220
„ „ „ by X-rays alone	355
„ „ „ by Surgery and Radium	14
„ „ „ by Surgery and X-rays	25
„ „ „ by Radium and X-rays	44
„ „ „ by Surgery, Radium, and X-rays ...	6

The following reports have been received, summarising the results of treatments carried out with Radium or Radon (or in some cases X-rays) during the year.

Report by Oswald J. Murphy, M.B., B.Ch.

St. Vincent's Hospital, Dublin.

The majority of the cases were treated by needles containing radium salt. Owing to shortage of hospital accommodation the number treated in St. Vincent's has fallen considerably, and as a result most of the patients were extern, or treated in private nursing homes.

MALIGNANT CASES.

Treated by Surgery and Radium	6
Treated by Radium and X-rays	3
Treated by Radium alone	85
Total, ...	94

Carcinoma of the ear, 3. No glands, 2; apparently well, 2. Glands, 1; improved, 1.

Carcinoma of the lip, 10. No glands, 6; apparently well, 6. Glands, 4; improved, 3; not improved, 1.

Carcinoma of the cheek, 1. No glands, 1; apparently well, 1.

Carcinoma of the parotid, 2.

Carcinoma of the tongue, 5 (no glands 2, glands 3). Anterior third, 3; well, 1; improved, 1; not improved, 1. Middle third, 1; improved, 1. Posterior third, 1; improved, 1.

Carcinoma of the floor of the mouth, 2. Glands, 2; improved, 1; not improved, 1.

Carcinoma of the tonsil, 1.

Carcinoma of the bladder, 1.

Carcinoma of the uterine cervix, 9. Group, I, 6; well, 6. Group II, 2; well, 1; improved, 1. Group III, 1; improved, 1.

Carcinoma of the uterine body, 2.

Carcinoma of the skin surfaces, 25. No glands, 24; well, 16; improved, 7; not improved, 1. Glands, 1; not improved, 1.

Rodent ulcers, 33. Well, 30; improved, 2; not improved, 1.

NON-MALIGNANT CASES.

Exophthalmic goitre, 1. Hodgkin's disease, 1. T.B. cervical glands, 4. T.B. peritonitis, 10. Uterine hæmorrhage, 2. Angiomata, 16. Lupus vulgaris, 2. Lupus Erythematosus, 3. Keloids, 6. Dupeytron contraction, 2. Pruritis vulvae, 2. Warts, 27. Total, 76.

Report by Oliver Chance, M.B., B.Ch., D.M.R.E.

Richmond, Sir P. Dun's, Dr. Steevens', Rotunda, and Coombe Hospitals.

Owing to unforeseen circumstances it is impossible this year to do more than give a list of the patients treated during 1939. Most of the cases requiring radiation, seen in the above hospitals, were referred to St. Anne's Hospital for treatment, and the bulk of the cases included below were either private cases or else those suffering from conditions for which they could be treated as out-patients. The instalment of a contact X-ray plant during the year has meant a very considerable increase in the number of cases treated with X-rays and a large decrease in the number of cases treated with radium.

MALIGNANT CASES (88).

Number of cases of all types of malignant disease seen during 1939	94
" " " " " treated during 1939	88
" " " " " treated by Surgery alone ...	8
" " " " " treated by Radium alone ...	3
" " " " " treated by X-rays alone ...	55
" " " " " treated by Surgery and Radium ...	2
" " " " " treated by Surgery and X-rays ...	16
" " " " " treated by Radium and X-rays ...	3
" " " " " treated by Surgery, Radium, and X-rays	1

TOTAL MALIGNANT CASES TREATED BY RADIATION (80).

Rodent Ulcers	26	Nasopharynx	1
Skin	3	Intrinsic Larynx	3
Lip	7	Extrinsic Larynx ...	3
Tongue	5	Oesophagus	3
Gum	3	Prostate	2
Palate	1	Rectum	0
Breast	11	Lungs	2
Cervix	1	Hodgkin's Disease ...	4
Body of Uterus	2	Myologenous Leukæmia ...	1
Vulva	0	Sarcoma	1
Ethmoid	1		

TOTAL NON-MALIGNANT CASES (TREATED WITH X-RAYS, RADIUM, OR RADON).
Toxic Goitre, 12. Naevi, 7. Various benign conditions, 15. (34.)

Report by Dr. R. E. Tottenham,

City and County Hospital, Londonderry.

Carcinoma of the cervix uteri. 3 cases. All were approximately late second group.

The Paris School aim at giving a dose up to 8,000 to 9,300 mc. h., but given at one application; using about 66 mg. of radium, I have aimed at the same total dosage, but giving it in three sittings at weekly intervals. Thus, 3,000 (odd) first application, 2,000, second, and 3,000 (odd) the third, according to the patient's tolerance. The first and third applications are both uterine and vaginal in the proportion of say 30 mc. uterine to 40 mc. vaginal. The second application was purely vaginal, about 50 mc. being used. I use a bored-out brass rod of necessary thickness for uterine insertion. For the vagina I use my own applicator, which is shaped like a tiny shell case, and having a little chamber at the end for the capillary tubes. The chamber is screened anteriorly and posteriorly by lead, below; so that the patient only receives those rays which are going up the long axis of the vagina.

The immediate result in all cases was satisfactory.

Carcinoma of the vulva. Ulcer size of a shilling on the left side.

First application, 27/1/'40. 24 mc., in nine needles. Dose received was about 500 mc.h., owing to many of the needles having fallen out.

Second application, 3/2/'40. 34 mc., in four needles. Dose 2,194 mc.h.

The ulcer was practically healed on leaving hospital.

Report from St. Anne's Hospital, Dublin.

Radiologist: Dr. Oliver Chance.

Malignant Cases.

Seen for the first time during 1939, and treated with radon or radium element.

Rodent Ulcers	33	Carcinoma of Oesophagus	1
Carcinoma of Skin ...	8	„ Colon ...	1
„ Lip ...	27	„ Rectum ...	2
„ Tongue ...	30	„ Uterus (Body)	2
„ Floor of Mouth	8	„ Uterus (Cervix)	28
„ Alveolus ...	3	„ Ovary ...	1
„ Cheek ...	2	„ Breast ...	6
„ Palate ...	2	„ Glands (secondary)	3
„ Fauces ...	3	Melanoma	1
„ Tonsil ...	1	Sarcoma	1
„ Epiglottis ...	1		
„ Maxillary Antrum ...	1	Total, ...	165

NON-MALIGNANT CASES.

Seen for the first time during 1939, and treated with radon or radium element.

Endometris	...	1	Angiomatous Naevi	...	2
Myomata	...	1			
Papilloma Penis	...	1			–
Cavernous Naevi	...	4	Total,	...	9

No major alteration in technique has occurred in 1939. The tendency for X-rays to replace radium in the treatment of certain conditions, noted in a previous report, is now even more obvious. The contact X-ray plant has now been in use for over three years, and there can be no doubt that in all suitably chosen cases of superficial malignant disease of the skin and lips, it can achieve just as good results as radium, and at considerably less cost in time, bed-occupation, and money.

We are now using deep X-rays as a "trial" treatment in many advanced cases of cancer of the mouth. If the reaction to treatment is watched closely, it is frequently possible, before the patient has been caused much discomfort, to decide whether treatment should be completed with X-rays alone, whether radium should be used, or whether it is wiser not to complete treatment. In this way many advanced cases are saved the severe discomfort and misery of intensive radiation, and at the same time the disease can be made to disappear in a few cases in which cure would have been impossible if radium alone were used.

In conclusion, we would thank the Staff of the Radon Laboratory for their efficiency and courtesy during the year.

No. 28.

THE PRODUCTION OF SANTONIN FROM IRISH-GROWN ARTEMESIA.

By PETER J. DRUMM, Ph.D., D.Sc.,
AND
WILLIAM F. O'CONNOR, M.Sc.

[Read May 28. Published June 13, 1940.]

The importance of a fine-chemical industry, based on the utilisation of native raw materials, is widely recognised nowadays. As the basis of many pharmaceutical chemicals is the coal-tar product phenol, the prospects for such an industry in Ireland would appear at first sight to be rather obscure. However, a number of chemical products which find a market in this country are of vegetable origin and thus embrace an industry which has a close relationship to our basic industry agriculture.

A definite tradition formerly existed in Ireland with regard to the study and use of herbs of medicinal value. A treatise on Irish herbs is contained in the volume by Threkeld printed in Dublin in 1727. In this is given a short account of native plants and "an abridgement of their virtues." To quote a more recent instance, the growing of Hyoscyamus and Belladonna was carried on about 1890 near Crumlin, Co. Dublin. The plants were sold to the Apothecaries' Hall of Ireland and processed at their laboratories at Chapel Lane, Dublin. The extracts of these plants found a ready market here and in England.

The present paper deals with the drug santonin, extensively used in medicine as an anthelmintic. It is the active principle of several species of Artemesia (Compositae), the most important of which is *Artemesia cina.* This latter grows abundantly in the wild state in Russian Turkestan, where the unexpanded flowerheads of the plant are collected, dried, and exported to England and other countries for extraction of the santonin. A second variety, *Artemesia brevifolia,* is found in the Himalaya region near Kashmir at altitudes of 4,000–10,000 feet, mostly in dry valleys. A hybrid variety of Artemesia is found on the west coast of Ireland and in particular in the estuary of the river Shannon.

As a preliminary to the present work samples of these plants were collected in the vicinity of Foynes, Co. Limerick, and extracted by a method described later in this paper. They were found to contain very little santonin. It was decided, therefore, to carry out experiments on the propagation of the plants from seeds of *Artemesia cina* procured from the Continent.

Cultivation of Artemesia cina.

Reliable information as to the best method of cultivation being very difficult to obtain, it will be appreciated that the following account is to be considered as of a preliminary nature.

The following is a report from Mr. H. Glavin, Head Gardener, University College, Cork, who had charge of the cultivation, and to whom the authors wish to express their indebtedness:—"The seeds were sown in boxes in the early part of April, 1938. When the plantlets were past the cotyledon stage, light and air were given freely, and soon afterwards they were transplanted into boxes about 3 inches apart. Towards the end of May they were transferred to drills, and the plants placed about one foot apart. These drills had been prepared with farmyard manure and a little artificial manure which consisted of a mixture of superphosphate, 4 parts, sulphate of potash, 2 parts, sulphate of ammonia, 2 parts. Some of the plants had produced flowerheads in September, 1938, and these were clipped with a shears in October. From the commencement of the growth period in the spring of 1939 the plants grew rapidly, and early in September yielded a good crop of flowerheads."

Artemesia cina is silver grey in colour, contains only a little chlorophyll, and exhales a characteristic odour. It has a tufted appearance, and when fully grown reaches a height of from 1·5 to 2 feet. It is somewhat procumbent in habit, and the woody stems are surmounted by tufts of small pinnatisect leaves. Flower development is slow. The plants appear to be of a hardy nature, as during the second year of growth they survived a severe period of frost.

Extraction of Santonin.

The best time for the harvesting of the plants is when the flowerheads are half opened, because at this stage the content of santonin is greatest.

The Artemesia were clipped with a shears and dried, forthwith, at a temperature of 50° C. in an electric oven, through which a current of air was circulated by means of an electric fan. When drying was completed the woody major stems were rejected. The flowerheads were then reduced to a coarse powder, and their santonin-content determined by the method of Massagetov (Khim, Farm. Prom., 1932, No. 2–3, 68–71).

20 g. of powdered flowerheads were rubbed in a mortar with as much of a solution of lime-water as contained 1 g. of calcium hydroxide. The whole was transferred to a beaker, 250 c.c. of distilled water added, and boiled for 10 minutes. The mixture was next filtered immediately through a Büchner filter, and the residue washed with hot water until the combined filtrates had a volume of 500 c.c. The warm filtrate was transferred to a separating funnel, and acidified by addition of 20 c.c. of hydrochloric acid of density 1·12. After cooling, the acid solution was extracted, first with 50, then with 30, and finally with 20 c.c. of chloroform. The combined chloroform extracts were then filtered into another separating funnel, and the new filtrate shaken with 50 c.c. of a 4 per cent. solution of sodium hydroxide to remove resin acids and other impurities. The chloroform layer, after separation, was washed with water, and then shaken with 0·2 g. of animal charcoal. Finally it was filtered into a 300 c.c. Erlenmeyer flask. The chloroform was removed on the water bath, the residue dissolved in 2 c.c. of absolute alcohol, and 100 c.c. of boiling water added. This solution was concentrated to a volume of 50–70 c.c., and then

set aside in a dark place. After 24 hours the santonin had crystallised. The crystals were collected and dried at 100° C. To the weight of santonin so obtained was added the standard correction of 0·0002 g. for every cubic centimetre of the filtrate.

The average yield of santonin, based on some ten estimations, was 0·75 per cent., calculated on the weight of dried flowerheads. Other methods of extraction gave a higher yield of santonin, in some cases over 1 per cent., but the purity of the product was inferior to that obtained by the method of Massagetov. The crude santonin obtained by this method melted at 169–171° C., and after one recrystallisation from aqueous alcohol the melting point rose to 173° C. A sample of the drug as used in pharmacy melted at 173° C. alone or when mixed with a sample of santonin from Irish Artemesia. The chemical identity of the two samples is thus established. A further check on the identity of the two samples of santonin was provided by comparison of their optical rotations. This was measured in a Schmidt and Haensch polarimeter, using a 1·4 per cent. solution of each in absolute ethyl alcohol.

$$[\alpha]_D^{18} \quad \text{(Santonin B.P.)} = -172°,$$

$$[\alpha]_D^{18} \quad \text{(Irish Santonin)} = -171{\cdot}5°.$$

A sample of Irish santonin, recrystallised from alcohol, was submitted for a pharmacological assay to Dr. F. Dyer, of the College of the Pharmaceutical Society, University of London, who carried out the following biological comparisons with a sample of santonin of B.P. quality:—

(1) The extent of inhibition of the normal muscular contractions of earthworm muscle.

(2) The extent of cardiac slowing of the isolated frog-heart.

(3) Toxicity on earthworms.

The following is an extract of the report received:—

"The biological tests showed that the sample was slightly less potent than the sample used as standard. Allowing for biological variations, it is concluded that the potency of the sample submitted is not less than 90 per cent. of that of the standard."

SUMMARY.

Artemesia cina, the source of the anthelmintic santonin, has been successfully cultivated in this country from imported seeds. The chemical and pharmacological identity of Irish santonin with that used in pharmacy has been established. Further experiments are being carried out with a view to determining the influence of such factors as soil, location, etc., on the yield of santonin.

The authors gladly acknowledge the loan of a polarimeter from the Royal Dublin Society. Thanks are also due to the Governing Body of University College, Cork, for a grant which has defrayed the expenses of this investigation.

CHEMISTRY DEPARTMENT,
UNIVERSITY COLLEGE,
CORK.

No. 29.

A MOLECULAR CONSTANT FOR SOURED MILKS. II. EFFECT OF PRESERVATIVES.

By J. J. RYAN and G. T. PYNE

(Department of Dairy Chemistry, University College, Cork).

[Read May 28. Published separately June 18, 1940.]

In previous numbers of these Proceedings (1), (2) we described the calculation and use of molecular constants for fresh and sour milks, based on simple analytical determinations. These constants can replace without great loss of accuracy the freezing-point method of estimating added water in milk. As that for soured milks is, however, limited to samples of not more than 3–4 weeks old, it seemed desirable to examine the possibility of extending this time range through the employment of suitable preservatives or low temperature storage. The present note records the results of such investigations.

Of the analytical determinations involved in the sour milk constant, the refractive index is the only one which is likely to be affected appreciably by souring conditions, use of preservatives, etc., and alone needs detailed consideration here.

In preliminary experiments conducted with the preservatives formaldehyde, mustard oil, and potassium bichromate, the last-named alone appeared promising. Attention was therefore confined to this preservative, which is, incidentally, the one commonly employed in Irish creameries when samples have to be held for fat analysis. Some experiments were also made on the effect of low-temperature storage without preservative.

Variations in Refractive Index.

(*a*) The presence of potassium bichromate, added at the usual rate of 1 commercial 5 gr. pellet per 4-oz. milk (lower concentrations proved relatively ineffective), was found to involve the use of 9·2 c.c. basic lead acetate per 100 c.c. milk, in place of the usual 5 per cent. or 6 per cent., in order to ensure a clear colourless serum in all cases. The table summarizes the departure from their initial values of the refractive indices (in degrees Zeiss) for a series of milk samples with and without preservative. Samples were held at ordinary temperatures. The use of bichromate has clearly greatly improved the constancy of the indices over these fairly long periods.

Sample .	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	Ran
Time held, days	23	30	30	31	31	40	40	42	42	42	47	50	50	50	56	61	
Change in R. Index																	
With preserv.	+0·05	+0·4	−0·05	+1·3	+1·25	+0·45	+1·2	+1·45	+0·75	+1·55	−0·2	−0·7	+0·95	+0·8	+0·3	+0·3	− 0· + 1·
Without	+0·45	+ 1·6	+1·7	+1·55	+2·8	+3·3	−0·25	+1·45	+2·25	+3·45	−0·55	−6·7	+2·25	+6·4	−2·3	+4·0	− 6· + 6·

(*b*) The holding of unpreserved milk samples at 0°–5° C. instead of ordinary temperatures proved ineffective to prevent considerable fluctuations in refractive index during storage. Thus, increases of 1·7, 3·8, 4·1, 4·2, and 4·9 degrees Zeiss were observed in five samples held 7–8 weeks at the lower temperature.

Analytical Methods.

The presence of bichromate in milk involves slight modifications in the methods (2) for chloride and phosphate. Chloride is determined by Drost's titration of a serum now prepared by diluting the milk with an equal volume of saturated barium nitrate, adding some crystals of sodium acetate to ensure precipitation of $BaCrO_4$, boiling ¼ hour, cooling, and filtering. For the total phosphate titration 1 c.c. 0·5 per cent. phenolpthalein is now added per 10 c.c. milk, and the standard end-point tint prepared by the addition of 5 drops 0·01 per cent. magenta to a further 10 c.c. of the same milk previously roughly neutralized.

The Molecular Constant.

For soured unpreserved milk this is approximately:

$$K = (R_s - R_w) + 2{\cdot}2\ (\text{c.c. } N/10\ AgNO_3/10\ \text{c.c. milk}) + 1{\cdot}6\ (\text{c.c. } N/10\ \text{acid}/10\ \text{c.c. milk}),$$

with an average value $K = 33{\cdot}5$ for unwatered milk (2).

The bichromate-preserved milks employed in the present work were found to yield sera whose refraction indices were on the average 1·0° Zeiss lower than those of the corresponding unpreserved samples. For unwatered milks

preserved with bichromate the appropriate value of K may therefore be taken as 32·5.

The usual deduction of 3 per cent. should be made from the percentage of added water calculated from the formula, $\frac{32{\cdot}5 - K}{K} \times 100$, in order to allow for natural variations of K for genuine milks. Owing to the general tendency of the refractive index to rise slightly during souring, this allowance will be in many cases equivalent to a somewhat higher one, calculated on the initial composition of the milk. A high degree of accuracy is not, however, in the nature of things possible with soured milks.

SUMMARY.

The determination of a molecular constant, with a view to controlling adulteration by watering, is possible for milk samples up to two months old which have been preserved with bichromate.

REFERENCES.

(1) RYAN and PYNE (1934).—Sci. Proc. Royal Dub. Soc., **21** (N.S.), 113.
(2) PYNE and RYAN (1937).—Sci. Proc. Royal Dub. Soc., **21** (N.S.), 581.

No. 30.

AWARD OF THE BOYLE MEDAL TO PROFESSOR JOSEPH REILLY.[1]

Professor Joseph Reilly's earliest work was published jointly with Professor Sir Gilbert T. Morgan, F.R.S., whose pupil he was. They studied non-aromatic diazonium salts and the mechanism of diazotisation; in these papers non-benzenoid diazonium salts were isolated and described for the first time. Much of his later work, in collaboration with his own pupils, has also been concerned with nitroderivatives and diazotisation. Proceeding to Cambridge with an 1851 Exhibition, Reilly worked on the resolution of asymmetric quinquevalent nitrogen compounds.

Having been appointed, early in 1915, as Chemist-in-Charge at the Royal Naval Cordite Factory, Holton Heath, Dorsetshire, he organised and directed the Laboratory with conspicuous success. The work was of a confidential nature, concerning explosives and the production of acetone and other solvents by a new fermentation method; several patents were taken out to cover this work. Later, he occupied the post of Head-of-Branch at the Research Department of the Royal Arsenal, Woolwich. Having become a recognised authority on certain explosives, he contributed, by request, about thirty articles (over 200 pages) to Worden's five-volume American work of reference: "The Technology of Cellulose Esters."

The knowledge of industrial distillation processes, which he acquired at Holton Heath, led to a request from the late Professor Sydney Young, F.R.S., to collaborate with Captain the Hon. F. R. Henley in writing the sections on acetone and alcohol in Young's standard work: "Distillation Principles and Processes."

At the end of 1925 Reilly was appointed to the Chair of Chemistry at University College, Cork, where he has not only maintained the academic reputation of the School of Chemistry for sound undergraduate teaching, but has built up a school of post-graduate research.

A list of the 136 books and papers of which he is the sole or joint author would show the very wide range of subjects in pure and applied chemistry dealt with, and the large number of students whom he has trained to collaborate with him in his work. That his researches should appear in no less than eleven standard journals, including German and Swiss, as well as British, is additional evidence of their wide range. Those published in our own Society's Scientific and Economic Proceedings include the important paper—with E. Ralph—upon the Phase System—Acetone, n-Butyl Alcohol and Water. In our publications, too, have appeared the work upon the thermal decomposition of peat and of coal, upon the investigation of polysaccharides, and upon the production of essential oils from Irish-grown plants.

Professor Reilly is still a comparatively young man, and we may look forward hopefully to a continuance of his activity in pure science and its applications to problems of economic importance.

[1] The Medal was awarded by the Council on May 11, 1939. It was presented to Professor Reilly by the President at the Stated General Meeting of the Society on December 7, 1939.

No. 31.

SALMON OF THE BALLISODARE RIVER.

I.—HISTORY OF THE BALLISODARE FISHERY.

By ARTHUR E. J. WENT,
Department of Agriculture, Fisheries Branch, Dublin.

(Plate No. 7.)

[Read 18 June. Published separately 16 August, 1940.]

Introduction.

In their reports for the years 1854, 1855, 1856, and 1858, the Inspecting Commissioners of Fisheries in Ireland drew attention to the fact that a number of small rivers in Ireland were at that time almost entirely unproductive, "the rights appertaining to them being divided amongst so many that no individual has a sufficient interest to induce him to protect or cultivate them." They compared these rivers to a common of land yielding little benefit to any one person, but which, if cultivated, would be productive of wealth to the country. Many of these small rivers were capable of producing a vast amount of salmon if the necessary authority existed to vest all the rights in one person or corporation.

The Inspecting Commissioners expressed an opinion that new sources of wealth might be produced by the adoption of some plan by which some enterprising person or corporation could acquire the widely scattered and ill-defined rights on a small river, and thus provide sufficient interest to carry out the necessary improvements and protection to convert the "barren" water masses into a valuable fishery. The Ballisodare[1] and Doohulla Fisheries were given as examples of the value of this work, and in the report for 1858 a detailed account of the early years of the Ballisodare Fishery was given. The story of the Ballisodare Fishery is therefore of great interest, since its early history can be followed fairly closely. The study of the age and growth of salmon of this river was considered highly desirable, and the opportunity was taken in 1938 and 1939 to obtain sets of scales and data from salmon captured in the net fishery in the tidal portions of the Ballisodare River. It is proposed in this paper to deal only with the history of the fishery, and to leave a description of the life-history of the salmon of this river until a later date.

[1] The spelling normally used in the town itself has been adopted throughout this paper.

(i) The Ballisodare River and its Watershed.

The name Ballisodare River is used to refer to the two and one-half miles of the river formed by the confluence of two fairly large rivers, the Owenmore and Arrow or Unshin River, which takes place about half a mile below the town of Collooney in Co. Sligo. This river has a catchment area of about 250 square miles, and empties into an inlet of Sligo Bay, called Ballisodare Bay, which forms its estuary. Some fairly high falls mark the boundary between fresh water and the tideway. These falls will be referred to in future as the Lower Falls, Ballisodare. For one-third of a mile above the tideway the bed of the river consists of a number of ledges of rock which produce a series of cascades or waterfalls, none of which is a serious obstacle to the passage of migratory fish. Just below the bridge in the town of Ballisodare there is a high fall, usually called the Upper Falls, Ballisodare. On the Owenmore River, about half a mile above its junction with the Arrow River, there is another series of impassable falls which reach a height of twenty-two feet.

The catchment area of the Owenmore River includes part of the Bricklieve and Curlew Mountains, whilst its tributary, the Owenbeg River, drains part of the northern end of Slieve Gamph or the Ox Mountains. Included in the catchment area of the Owenbeg are regions where heavy rainfall is prevalent, and hence this part of the Ballisodare River system is subject to heavy floods. At the head of the Arrow or Unshin River Lough Arrow forms a reservoir which conserves water to a certain extent, so that the Arrow is not so liable to sudden floods as the Owenmore River. The spate character of the Owenbeg River and its tributaries determines to a great extent the character of the two and one-half miles of the Ballisodare River. Although Ballisodare Bay is about 24 square miles in extent, the major part of this area consists of sand banks, so that at low tide only a series of narrow channels is left.

The major part of the watershed of this river consists of Carboniferous Limestone, which, as is well known, forms the great Central Plain of Ireland. Except for a few very small tributaries, which run over rocks belonging to the Devonian (Old Red Sandstone) and the lower beds of the Carboniferous series, the Owenmore and Arrow Rivers drain areas of limestone. In consequence the waters of these rivers are highly alkaline; the fact that the pH of the waters of Lough Arrow and Arrow River under ordinary circumstances is 8·0 is a good indication of this. The Owenbeg River and its tributaries drain part of the northern end of the Ox Mountains, which are made up of metamorphic rocks (Gneiss and Mica Schists) containing little or no lime, and the waters of this river vary considerably in character, mainly depending on the weather conditions. The character of the Ballisodare River depends to a great extent on the relative flows of the Owenbeg and of the other rivers. As mentioned previously, the Owenbeg is subject to sudden floods, and it often happens that heavy rainfall on the Ox Mountains suddenly puts the Owenbeg River into flood, and the admixture of large quantities of acid water with the normal alkaline water of the Owenmore River considerably lowers the

pH of the water of the lower part of the Owenmore and of the Ballisodare River itself. Fig. 1 shows the relationship of the various rivers, and the geology of the watershed.

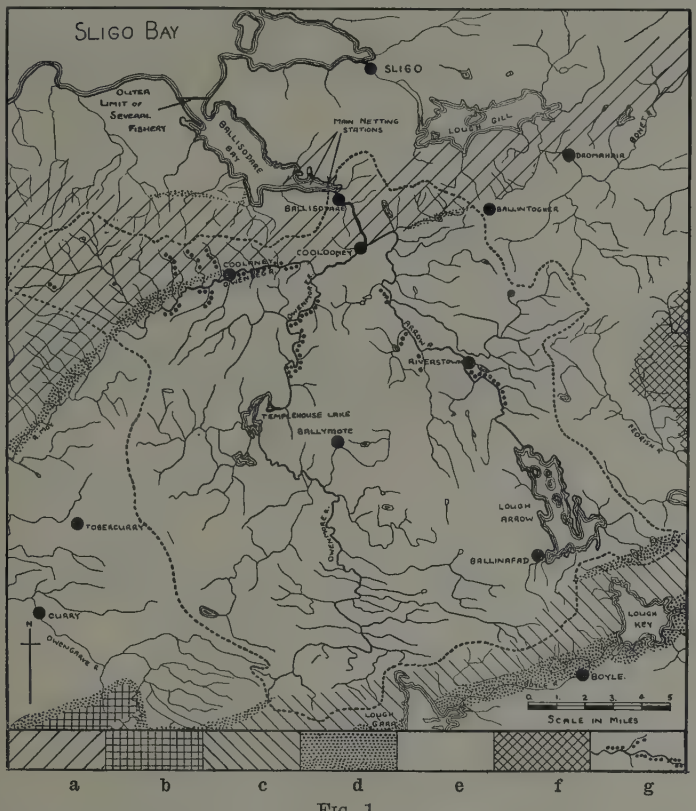


FIG. 1.

Based on the Ordnance Survey by permission of the Minister for Finance for Ireland.

(a) Mica Schists and Gneiss. (b) Upper Silurian. (c) Old Red Sandstone (Devonian). (d) Lower Carboniferous Sandstone. (e) Upper, Middle, or Lower Carboniferous Limestone. (f) Lower Coal Measures, Millstone Grit, or Yoredale Beds. (g) Spawning reaches indicated thus.

(ii) THE FISH PASSES AND THE OBSTRUCTIONS IN THE RIVER.

Prior to 1852 a 22-feet barrier of rock at the head of the tideway barred the passage of salmon into the Ballisodare River, and only a score of salmon were taken annually in the pool at the foot of these falls. Salmon attempted to ascend the falls at a place near the east bank (Plate 7 B). The more athletic fish apparently managed to reach the first ledge, but owing to the small depth of water there they were unable to progress any further, and were washed back into the tidal pool below. Even to-day salmon often make attempts to ascend

the falls in the angle on the east bank. When they fall back into the tidal pool, however, they readily find the entrance to the fish pass.

The fish pass at the obstruction formed by the Lower Falls was completed in the year 1852, and was the first large successful fish pass to be constructed in Europe. This pass is divided into 20 pools, as may be seen from Fig. 2,

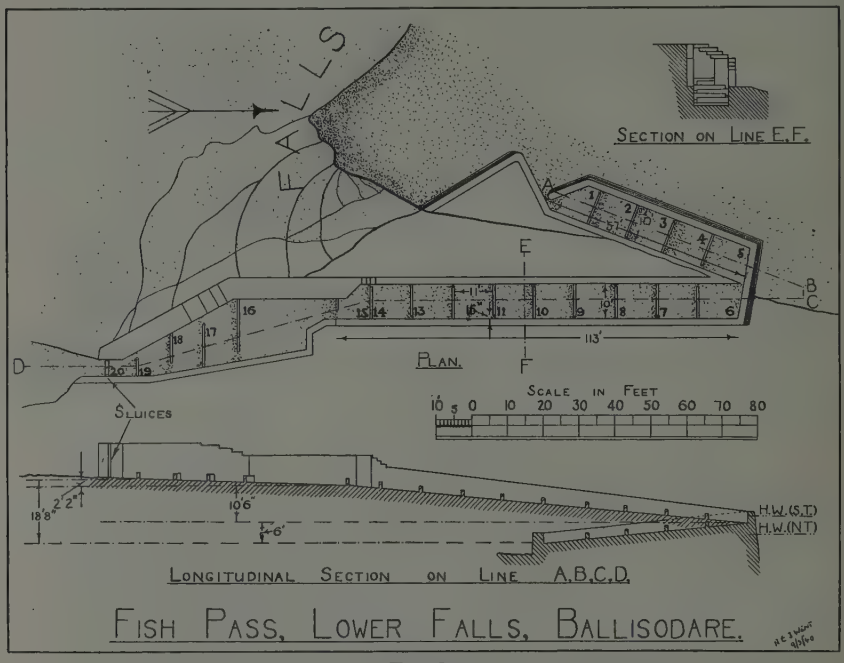


FIG. 2.

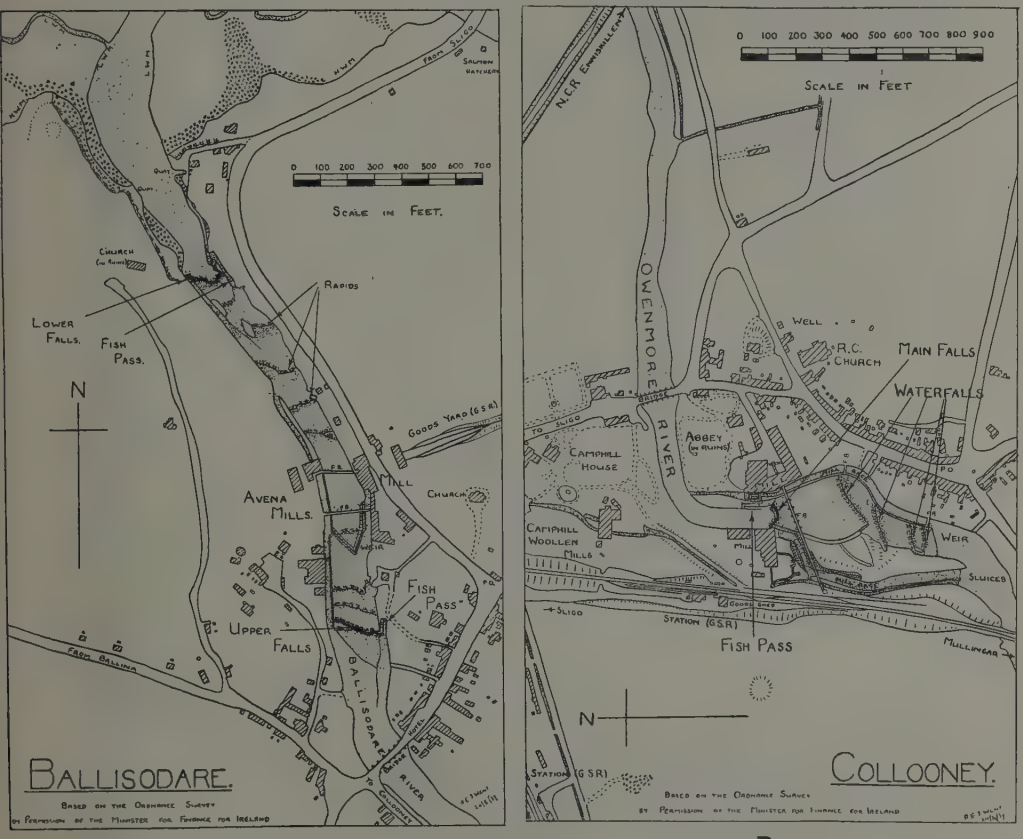
PLAN AND SECTIONS OF THE FISH PASS AT THE LOWER FALLS, BALLISODARE.
Shaded portion of plan indicates area of water at times of medium floods.

and of these the upper 15 pools are in the same line. The remaining 5 pools are turned back in an upstream direction, so that the entrance to the pass is close up to the falls. Salmon have no difficulty in finding the entrance, which is situated quite near the place where they usually lie below the falls. An overall length of approximately 248 feet, affording a passage over an obstacle about 19½ feet high, gives an average incline of about 1 in 13. As the upper 5 pools are on an incline of 1 in 30, the remainder of the pass has an incline of 1 in 10. The purpose of the upper pools was, apparently, to diminish the speed of the water as it enters the pass, particularly during periods of floods. Part of the pass is constructed of large slabs of roughly hewn local stone, and pools 7 to 12 were blasted out of the solid rock (limestone). The pools are 10 feet wide, the middle series (Nos. 6 to 14) are about 11 feet long, whilst the lower pools (Nos. 2 to 4) are about 12½ feet long. The spur walls are 18 inches

high, and slope slightly towards the gap. Gaps 15 inches wide on alternate sides of the pools in the lower part of the pass extend to the floor of the pass. Therefore in ascending this pass no jumping is necessary on the part of any salmon.

Two sluices at the head of the pass, each 2¼ feet wide, are used to control the amount of water entering the pass, and by frequent adjustment of these the maximum efficiency is attained.

Between the Lower and Upper Falls at Ballisodare the bed of the river forms a series of ledges in the Carboniferous Limestone. In this way a series of rapids is produced, none of which is, however, a serious obstacle to the



A B

FIG. 3.

passage of ascending salmon in normal water conditions. In Fig. 3 A the main ledges between the Upper and Lower Falls at Ballisodare have been indicated.

The Upper Falls, Ballisodare, are situated about a quarter of a mile above

the head of the tideway, and are about 9 feet high. Although at the time of the construction of the first fish pass here in 1853 they were considered to be a serious obstacle to the passage of salmon, to-day they can be passed by the majority of fish. Whether the statement made in 1858 (Commissioners, 1858) that the Upper Falls were originally impassable to salmon was based on an imperfect knowledge of the powers of salmon, or whether subsequent changes in connection with Avena Mills (Fig. 3 A) made the ascent of these falls easier, it is difficult to say, but certainly Mr. Cooper, the originator of the plan to improve this river, and his advisers considered it necessary to build a fish pass at this place. Indeed, they even went to the trouble of reconstructing the original fish pass because fish had difficulty in finding the entrance.

No plans are available of the original fish pass to provide a passage for salmon over the Upper Falls, Ballisodare, but it is clear from Mr. E. J. Cooper's report to the Commissioners of Fisheries in 1858 (Commissioners, 1858) that the outlet from this pass was too far below the falls and salmon missed the entrance. Apparently the original pass here consisted of a number of pools placed in one straight line. Reconstruction of the pass was carried out by bringing the entrance under the fall itself. With the exception of the controlling sluice at the head of the pass which is now missing, the fish pass is in the same condition as when it was completed in the year 1855. The present pass consists of 12 pools of varying shapes (Fig. 4), and its entrance is situated immediately under the flag which forms the overhanging sill of the fall. The situation of the entrance to the pass is indicated in Plate 7 (d). To

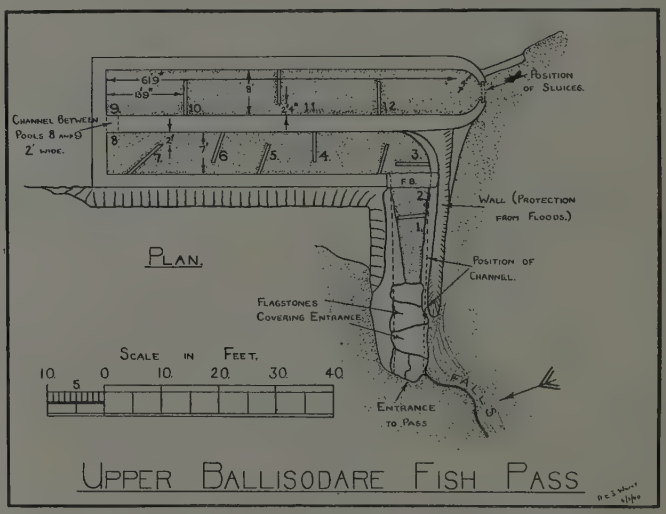


Fig. 4.

Fish Pass at the Upper Falls, Ballisodare.
Ordinary water levels shown dotted.

enter the pass proper a fish must negotiate a tunnel 15 feet long. This tunnel consists of a deep channel cut in the solid rock covered over with heavy flagstones. Pools 1 to 8, inclusive, are of varying sizes and shapes, and the spur walls are set at a variety of angles to the side walls of the pass. In the lower part of the pass (pools 4 to 8) the gaps are 2 feet wide and are continued to the floor of the pass. The gaps in the spur walls of pools 9 to 12, inclusive, are 2 feet 4 inches wide. A channel 2 feet wide, which is covered by a flagstone, affords the connection between pools 8 and 9. An overall length of approximately 132 feet and a rise of about 9 feet gives an average incline of nearly 1 : 15. When first constructed the pass was provided with sluices at the head to control the quantity of water flowing through it. By the year 1870 it was decided that the Upper Falls were not so serious an obstacle to ascending fish as was first imagined (Francis, 1870). To-day the bulk of the salmon make their way without difficulty up these falls on the opposite bank to the fish pass (Plate 7 (d)). On that side of the river the falls consist of two subsidiary falls, each about 4 to 5 feet high. Summer fish, which form the bulk of the fish in this river, have no difficulty in ascending these two falls, particularly as they are coming fresh from the sea. An occasional spring fish early in the season finds difficulty in ascending these falls, and makes its way up the fish pass. Even if the fish pass here had not been constructed, it is unlikely that salmon would have found this series of falls a serious impediment in their passage upstream.

At Collooney on the Owenmore River, about a half-mile from its junction with the Arrow River, another set of falls exists. Although somewhat less in height than the Lower Falls, Ballisodare, they are much more imposing in consequence of their precipitous character (Plate 7 (f)). Owing to the configuration of the ground the pass had to be gradually built up from the river bed in masonry. Large slabs of roughly hewn local stone were used here for the purpose. Having an overall length of 164 feet with a rise of 15½ feet, the Collooney pass is somewhat steeper than those at Ballisodare. It has, however, a valuable resting pool in the angle of the pass, so that, although a fish may almost exhaust itself in running the first series of six pools, which are set at an incline of about 1 in 9, the fish is given a chance to recover before tackling the remaining pools. In the upper part of the pass the ten pools are set at a smaller incline (1 in 11·8) than those of the first series, and these offer no great difficulty to the majority of fish. Pools 2 to 6 are 8′ 7″ wide, the resting pool, No. 7, which often gets filled with sand, is 15′ 9″ wide and 16′ 5″ long, and the remaining pools are 8′ 9″ wide. At the head of the pass a pair of sluices, each about 2 feet wide, controls the amount of water entering the pass. Again, the entrance to the pass is brought near the base of the falls, as can be seen in the sketch-plan given in Fig. 5 and in Plate 7 (f). The three upper spur walls in the pass were 20 inches high with gaps of 9 inches, and the rest were 19 inches high with gaps of 12 inches. After the pass was constructed it was found that the rush of water into the upper pools necessitated the raising of the height of the spur walls in pools 16 to 18 inclusive (Francis, 1870).

This was successfully accomplished by placing a plank 13 inches deep on top of the stone spur wall so as to extend completely across the pass, and a submerged orifice of 20 inches high and 9 inches wide was left. In recent years it was found that more efficient working could be produced by removing

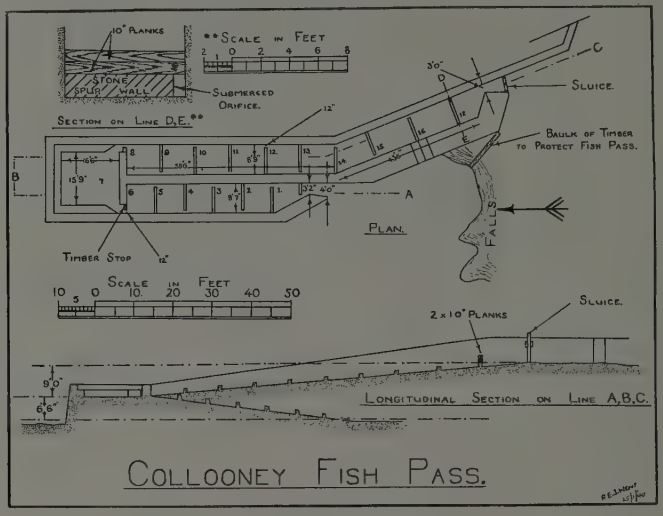


Fig. 5.

Plans and sections of the Collooney Fish Pass.

the planks on top of the spur walls in pools 15 and 16, and replacing the 13-inch planks on the top of the uppermost spur wall by two 9–10 inch planks, as shown in Fig. 5. Experience also showed that water in the resting pool (No. 7) did not stand at the required level. A small plank was placed in the outlet of the pool, and this had the desired effect of raising considerably the height of water in the pool, thus affording an adequate resting place for fish.

The Collooney fish pass was completed in 1853, and, apart from the modifications mentioned above, it is in the same condition to-day as when it was first erected.

Calderwood (1926) mentions that the Collooney pass did not answer very well at first, but after an alteration in the position of the entrance had been made it appeared to function satisfactorily. This statement appears to be based on a misunderstanding, as, according to Mr. Edward J. Cooper, only the fish pass at the Upper Falls, Ballisodare, was altered structurally. Both Calderwood (1926) and Schmidt (1906) give incorrect dates for the erection of the Ballisodare and Collooney fish passes.

Above the main falls at Collooney the river flows over a series of ledges in the Carboniferous Limestone which produce a number of rapids or small waterfalls (Fig. 3 B). None of these falls is, however, a serious obstacle to the

passage of salmon under water conditions in which fish would attempt to ascend the Collooney fish pass.

The fact that the Ballisodare and Collooney fish passes have withstood the ravages of almost 90 years with only minor repairs is greatly to the credit of their designer, one William Forsythe, an engineer to the Board of Works in Ireland.

The question has often been asked whether or not it was by a lucky chance that the fish passes at Ballisodare and Collooney have proved so successful. Hassard (1937), discussing the requirements for fish passes, states that a "fish pass, whether round, through or over an obstacle to the ascent of fish, should provide (*a*) either a swimming route not too steep, not too long (unless provided with resting pools), and containing smooth black—not white frothy—water, or (*b*) if it is necessary to ask the fish to jump, should provide a vertical rise at each jump that will be well within the capability of the less athletic fish, and with water below the rise of a depth ample to allow it to attempt the jump." We can now examine the fish passes at the Lower Falls, Ballisodare, and at Collooney in the light of these criteria. Both passes provided a swimming passage for salmon, since the gaps in all the spur walls are carried to the bottom of the pass; the route is not too steep (inclines from 1 in 10 to 1 in 13), but the majority of the pools contain white frothy water. It is well known that spring fish will not attempt to ascend obstructions by jumping early in the season, nor will they face a strong current of highly aerated water if the water is cold (a temperature of 5° C. or less). Summer fish, particularly grilse, will, on the other hand, usually face a rush of superaerated water. Calderwood (1926) states that fish passes at "obstructions which stop spring fish when the water is cold have to be very easy; have to contain black water and be without any place where a fish has to leap." It is highly probable that spring salmon, early in the year when the temperatures are low, would be loth to use the passes at Ballisodare and Collooney owing to the white frothy water they contain. The entrances of the two main passes are ideally situated, as they are placed quite close to where the fish lie below the falls. Although details of the age and growth of the salmon of the Ballisodare River are not yet available, it can be shown that, leaving the previously spawned fish out of consideration for the moment, almost 90 per cent. of the salmon of this river are summer fish running in the months May to July, inclusive, when the water temperatures are comparatively high. As was mentioned previously, such fish will readily pass through rough and broken water, and, therefore, they find no difficulty in ascending the two major fish passes on the Ballisodare and Owenmore Rivers.

We do not know what factors decide whether a river will have a run of spring (early) or summer (late) fish; but had it so chanced that the Ballisodare River was an early spring river, it is probable that these fish passes would not have proved as effective as they turned out to be. In this respect the success of Mr. Cooper's experiments, having as their aim the conversion of the Ballisodare River system into a salmon fishery, depended on a lucky chance.

There is no intention on the part of the author to belittle Mr. Cooper's achievement, but it seems essential to point out that, even with the more extensive knowledge available to-day, the promoter of a similar scheme for the transformation of a "barren" river into a salmon fishery must be prepared for complete failure or a very limited return for his expenditure.

(iii) The History of the Ballisodare Fishery.[2]

From time immemorial a few salmon were caught in the small pools in the tideway immediately below the Lower Falls at Ballisodare, and these pools constitute what was known prior to 1854 as the Ballisodare Fishery. The fish taken there were probably "strays" from the salmon rivers in the neighbourhood, which were travelling in search of their river of origin. Apparently the average number of salmon taken annually prior to 1854 in the tideway of the Ballisodare River did not exceed twenty.

On the 12th May, 1806, Joshua Edward Cooper acquired in fee-simple from Sir Edward Crofton, Baronet, the townland of Knockmuldowney, or Ballisodare, including the town of Ballisodare, together with the tolls and customs of the fairs and markets there, and "the salmon fishery and all the fisheries of the river commonly called the river of Ballisodare." This transaction may be said to be the prelude to the second era in the history of the Ballisodare Salmon Fishery.

Mr. Cooper conceived the idea of transforming the "barren" rivers of the Ballisodare system into a valuable salmon fishery[3] by constructing the necessary passages over the three obstacles mentioned previously. Mr. Cooper died in 1837, before these plans could be carried out, and was succeeded by a nephew, Edward Joshua Cooper.

It was considered in 1837 that the work planned could not be carried out without an Act of Parliament, and on the 30th June, 1837, the necessary legislation, "An Act to enable Edward Joshua Cooper to establish and protect a salmon fishery upon the lakes and rivers of Owenmore and Arrow and also within the Bay of Ballisodare in the County of Sligo in Ireland" (1 Vict., Cap. LXXXIX), was passed by the Parliament of the United Kingdom. The operative part of this Act enabled the salmon ladders to be constructed, enabled Edward Joshua Cooper to purchase the several fishing rights of any person or Corporation in possession of them, and provided that on payment of the purchase money all such rights should be vested in the said Edward Joshua Cooper. Further, it provided that the Bay of Ballisodare, the lakes and rivers of Arrow and Owenmore, and the several rivers and streams connected therewith, should be deemed to be the free (several) fishery of Edward Joshua Cooper, his heirs and assigns for ever. The Act also granted to Edward Joshua

[2] Compiled from several sources, including Commissioners, 1858, Irish Law Reports, 1935, Statute, 1837, and O'Rourke, 1878.

[3] This was referred to in the Sixth Report of the Commissioners of Irish Fisheries for the season of 1824. Dublin, 2nd June, 1825.

Cooper the sole and exclusive right of catching salmon and other sea fish within Ballisodare Bay, rivers, and lakes, and made it a penal offence for any other person without a licence from the owner to fish for salmon or other sea fish in this area; the right of the proprietors of the "banks" of the bay, rivers, and lakes, to fish for salmon and other sea fish with rod, line, and fly only, being reserved. The latter rights were later acquired by the Cooper family. The limit of Ballisodare Bay was also defined (Fig. 1). Further provisions were made for the protection of the fishery, and for dealing with wilful damage to the fish passes. An Act passed five years later, 5 & 6 Vict., Cap. 106, 1842, repealed part of the "Cooper Act" in so far as Edward Joshua Cooper, his heirs and assigns could use or exercise only those rights which could be lawfully enjoyed, used or exercised by the proprietors of any similar fishery by virtue of the provisions of the new Act.

After the passing of the enabling Act Mr. Cooper negotiated with the owners of the lands surrounding Ballisodare Bay for the conveyance to him by deed of their fishing rights therein for a nominal sum, said to be five shillings. The majority of these gentlemen made the necessary conveyance to Mr. Cooper of any rights they believed they possessed, but two gentlemen, the joint owners of the townland of Abbeytown, Roger and Thomas McManus, held out for a higher sum. Eventually, after several years' delay, it is said that they were paid the sum of £350 for any rights they may have possessed in the matter.

Whilst negotiations were proceeding for the acquisition of the fishing rights in the bay Mr. Cooper began a series of experiments with a view to stocking the Arrow River with salmon. In the years 1837, 1838, and 1839 salmon caught in the pools below the Lower Falls were placed in the river above Ballisodare Bridge. The total number of fish dealt with were—9 fish weighing 54 lbs., 15 fish weighing 75 lbs., and 16 fish weighing 80 lbs., in the three years respectively. Careful watch during 1838, 1839, and 1840 did not reveal any signs of salmon fry or spent fish, and up to 1846 no increase in the number of fish below the Lower Falls at Ballisodare was observed. In 1846 18 fish were transported above Ballisodare Bridge, and in 1848 a few fry were believed to have been observed. The falls at Collooney on the Owenmore River prevented fish from ascending that river, so that only the Arrow River could have been stocked with salmon. Nevertheless, it was obvious that these experiments were failures.

In 1851 another series of experiments was carried out, and for the sake of convenience a summary of the events in each year is given below.

1851.

On the 24th December three pairs of fish were obtained from the River Moy and were placed in the Owenbeg River about 7 miles above the Falls at Collooney. A small quantity of fertilised ova (amount not stated) was also deposited in the same river two days later.

1852.

The fish pass providing a passage over the obstacle formed by the Lower Falls at Ballisodare was completed. Six fish were taken above the fish pass and transported over the Upper Falls.

1853.

A few fish were transported over the Upper Falls. The fish pass at Collooney was completed, together with the original pass at the Upper Falls. The latter pass did not function satisfactorily, as apparently the entrance to the pass was too far below the main fall. Large numbers of salmon fry were seen above the Collooney Falls, and numbers were taken on trout rods before their identity could be established. By the 17th May many of the fry had left the river. These fry must have been derived from the three pairs of salmon and the small quantity of ova put in the Owenbeg River in December, 1851.

1854.

Fish commenced to run up the river in May, and passed up the fish pass at the Lower Falls quite satisfactorily. The pass at the Upper Falls was being rebuilt, as the old one was not successful. Below the Upper Falls a draft net was used, and 179 fish, the majority of which were grilse, were obtained. These fish, together with 77 sea trout, were put above the Upper Falls, and for the first time fish could ascend to the upper waters of the Owenmore and Owenbeg Rivers.

1855.

The new pass at the Upper Falls was completed and functioned satisfactorily. Several spent fish were observed returning to the sea in the early part of the season. Fishing on a small scale was carried out, and 188 salmon, averaging 5 pounds each, were taken. Several salmon were found dead on the spawning beds having been killed by otters.

1856.

Large numbers of fry were seen in April and May. One spent fish which had been marked in the previous season was taken. It had been marked as a spent fish in the early part of 1855, and it was estimated that its weight in good condition at the time of its second capture would have been in the neighbourhood of fourteen pounds. Fishing was only carried out on 13 days, and 18 fish, averaging 7 pounds, were taken.

1857.

The first grilse appeared on the 26th June at the Lower Falls. There were no spring fish. Grilse were plentiful by the 1st July and continued so until the end of the season. Very few large fish were seen. No fishing was carried on during this year. On the 19th December one of the fishermen caught two fish about 4 pounds weight, each of which had been marked as fry in April,

1856. Mr. Cooper in his notes (Commissioners, 1858) states that he had not observed any fry that he had marked in the same spring. An inspector was appointed for the fishery, and his diary indicated that observations at the three fish passes and of the river showed that there was a good stock of salmon present.

1858.

Fishing from February to 1st July was only carried on spasmodically and 49 fish were taken during that time. 868 fish were taken in July, 530 in August up to the close of the season on the 20th day. These fish averaged 4 pounds each.

Archdeacon O'Rourke in 1878 gives the following catches of salmon:— 1859, 2,000 fish; 1861, 3,000 fish; 1862, approximately 4,000 fish; and 1863, 6,000 fish. He also states that the maximum number of fish taken during one season was 11,000, and that the average for the few seasons preceding the publication of his book was about 8,000 to 9,000. Up to 1878 the greatest number taken in one day was 1,400 fish, and the greatest draught was 600 fish. Francis in 1870 mentions that in 1869 the catch was 9,750 fish.

The new era in the history of the river appears to date from 1853, when the three fish passes had been completed, and a large number of fry were seen in the stretch of the river above Collooney below the junction of the Owenmore with its tributary the Owenbeg River. In the year 1854 179 fish (169 of which were apparently grilse) and 77 sea trout were put over the Upper Falls at Ballisodare, as the pass there was not functioning satisfactorily. Before the beginning of the salmon runs in 1855 this pass was reconstructed, and a free run of fish was then permitted to the upper reaches of the river.

Some spent fish were seen dropping down in the spring of 1855 and 1856, and the presence of appreciable quantities of fry in 1856 and 1857 indicates that fairly effective spawning had taken place in 1854 and 1855. The contemporary report referring to these fry stated that "at first they were brown, with spots like finger marks on their sides; in May many were silver coloured, and had lost the spots on their sides; yet there were still many of the brown ones." It appears, therefore, that only part of the progeny of the 1854 fish migrated to the sea as one-year old smolts. The reports (Commissioners, 1858) lead us to infer that the 1854 runs of fish were mainly the returning survivors—as grilse—of the 1853 fry, which were seen in large numbers in the stretch of the river between Collooney and the junction of the Owenmore and Owenbeg Rivers. These reports emphasize that prior to 1853 no salmon could have got beyond the Falls at Collooney. The conclusion is reached that these fry were the produce of the three pairs of salmon transported from the River Moy, and of the small quantity of ova from an unknown source deposited in the Owenbeg River in 1851. As nothing was done to assist salmon over the falls at Collooney between 1846 and 1851, and as there was no laying down of ova previously, we must accept this conclusion. It is not impossible that some of the fry seen in 1853 were smolts resulting from the ova deposited

in the autumn of 1851 and hatched out in 1852. The records do not show the weights of the three pairs of salmon introduced from the River Moy, but if they were 20 pounds each (this would be a good fish for the Moy) the total yield of ova would not exceed 48,000, or with the additional "small" quantity of ova placed in the river at the same time, a total of 60,000. It is exceedingly surprising that smolts derived from this number of ova were in sufficient numbers to produce a run of returning adults in 1854 adequate to populate hitherto "barren" waters to the extent of establishing a prolific and profitable fishery in such a short time, for by the year 1857 it seems clear that the run of fish was considerable. It is proposed to defer further discussion on this point until a later date, when the determinations of age and growth of the salmon of this river, as exemplified by the results of the examination of the scales from adult fish captured in the years 1938 and 1939, have been completed. In passing, it might be noted that the sea trout are not very plentiful in this river system, so that the putting of the 77 sea trout above the Upper Falls at Ballisodare in 1854 did not result in a prolific fishery for sea trout.

Archdeacon O'Rourke records that the erection of the necessary works, the purchase of the fishing rights and the Act of Parliament cost about £7,000.

(iv) Catch Records for the Ballisodare Fishery.

Unfortunately records of the catches at the Ballisodare Fishery are not available for the whole of the period from the year 1853 until the present time, but Mr. F. F. Scott, Manager of the Fishery, was kind enough to provide me with the catch figures which he had in his possession. These figures (given on the opposite page) are interesting, inasmuch as they illustrate the state of development of the fishery and the fluctuations in the catch over a fairly long period. In the years 1880, 1881, 1883, 1885 to 1888, 1896, 1903, 1930, 1934, and 1935, the catches were exceedingly high (140 per cent. of the average for the period 1896 to 1939 or more), whilst in the years 1904, 1907, 1908, 1910, 1913, 1916, 1920, 1928, and 1929, the catches were very poor (60 per cent. of the average or less); Fig. 6 illustrates graphically the fluctuations in the yearly catches. The average catches in the periods 1880 to 1888, 1896 to 1899, 1900 to 1909, 1910 to 1919, 1920 to 1929, and 1930 to 1939, were determined, and have been indicated in Fig. 6.

It will be seen from Fig. 6 that there is a gradual decrease from 1880 to 1888, reaching a minimum in the period 1910 to 1919, and thereafter an increase is observed. O'Rourke (1878) stated that by 1878 the average catch was about 8,000 fish (180 per cent. of average for period 1896 to 1939 inclusive); the maximum up to that time being about 11,000 fish. If these figures are correct, the decrease in the catches had already set in by the period 1880 to 1888. Francis (1870) states that the manager of the fishery, a Mr. Hepburn, informed him that the catch of 1869 was 9,750 fish, which was not exceeded in the years for which we have accurate figures (see record).

Record of net catches at Ballisodare for the period 1880 to 1888 and 1896 to 1939

Year	Number of Fish	Percentage of average (4413) for period 1896 to 1939 inclusive	Weight of catch in lbs.	Average weight in lbs.	Year	Number of Fish	Percentage of average (4413) for period 1896 to 1939 inclusive	Weight of catch in lbs.	Average weight in lbs.
1880	6,568	148.5	)	-	1910	2,594	58.9	16,664	6.43
81	6,296	142.2	)	-	11	4,125	93.6	24,960	6.06
82	3,597	81.6	)	-	12	3,154	71.6	20,462	6.48
83	9,212	208.5	)	-	13	2,426	55.0	16,201	6.68
84	4,247	96.4	)	-	14	3,430	78.0	19,661	5.72
85	7,665	173.5	) No	-	15	3,850	87.5	22,328	5.80
86	6,674	150.8	)records	-	16	1,933	43.9	11,504	5.95
87	7,400	167.3	)	-	17	3,592	81.5	25,418	7.10
88	8,223	186.0	)	-	18	5,809	131.4	31,214	5.37
89	)	-	)	-	19	3,014	68.7	19,180	6.37
1890	)	-	)	-	1920	2,169	49.2	13,709	6.32
91	) No	-	)	-	21	4,207	95.6	27,218	6.47
92	)records	-	)	-	22	4,673	105.8	27,070	5.79
93	)	-	)	-	23	3,928	89.1	24,622	6.27
94	)	-	)	-	24	4,450	100.7	26,585	5.97
95	)	-	)	-	25	5,519	124.8	31,576	5.72
96	7,713	174.5	40,245	5.21	26	5,140	116.2	38,035	7.42
97	4,845	109.5	23,575	4.82	27	3,524	80.0	25,398	7.22
98	2,925	66.4	12,158	4.17	28	2,567	58.3	18,154	7.08
99	3,037	68.8	18,621	6.13	29	2,271	51.6	18,283	8.06
1900	3,497	79.3	20,109	5.76	1930	6,916	156.5	40,329	5.82
01	3,203	70.3	18,050	5.63	31	7,678	83.5	52,618	6.86
02	5,627	127.3	36,730	6.53	32	5,850	132.2	39,830	6.83
03	8,880	198.5	51,696	5.82	33	5,856	132.3	39,488	6.73
04	3,299	47.8	20,292	6.17	34	6,841	154.7	45,330	6.64
05	3,514	79.7	21,690	6.18	35	6,765	153.0	43,708	6.47
06	5,672	128.3	31,887	5.62	36	5,384	121.8	37,788	7.02
07	2,382	55.1	13,345	5.60	37	4,456	100.8	26,702	5.18
08	2,148	48.8	12,185	5.67	38	3,151	71.6	21,187	6.72
09	6,063	137.0	34,954	5.77	39	6,107	138.2	39,836	6.52

The weights of the catches for each year in the period 1896 to 1939 were also available, and these are given in the table. It is quite clear from the average weight of the fish captured during this period, namely, 6·16 lbs., that the bulk of the fish were grilse. This has been confirmed by scale reading for the years 1938 and 1939. The average weight has shown an increase from 1896 until the present day, as will be seen from Fig. 6.

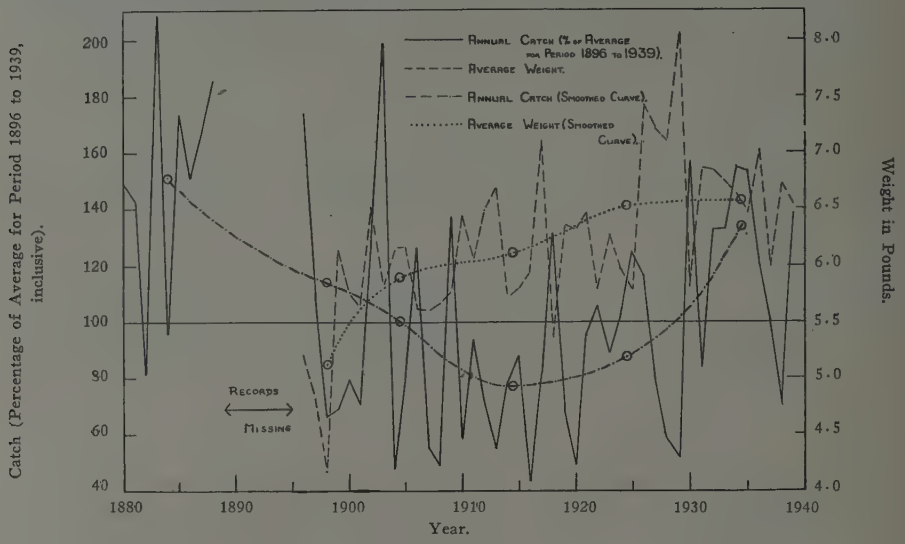


Fig. 6.

Fluctuations in the Catches and average Weights of Salmon taken in the Ballisodare Fishery.

No information is available as to the proportion of spring and summer fish in the catches in the Ballisodare Fishery over the period under review, but it is obvious that, although there may have been a slight increase in the proportion of spring fish during the period 1896 to 1939, the average weight of the grilse themselves has also increased.

In a previous publication (Went, 1938) it was mentioned that the number of packages of Irish Salmon offered yearly for sale at Billingsgate Market, London, was a good indication of the strength of the salmon runs in Ireland. Most of the salmon offered for sale from the beginning of June onwards consist of summer fish (grilse mainly, with a few small summer, previously spawned, and large summer fish). If these figures are examined it is clear that from the beginning of the century the numbers of summer fish have decreased until 1930, when they commenced to increase again. In the following table the average number of boxes of Irish Salmon offered for sale at Billingsgate Market from June onwards in 10 year periods is given. From about 1920 onwards there is evidence that a change in the size of the packages of Irish Salmon had

taken place. Before and during the European War (1914–18) the standard package of Irish Salmon contained between 120 and 140 lbs. of fish, but the standard package from the year 1920 or thereabouts appears to be one constructed to carry 100 lbs. Therefore in order to obtain more comparable figures the average number of packages for the first two periods have been increased by 30 per cent., and the weighted values are given in the last column of the following table:—

Period.	No. of Packages.	Weighted No. of Packages.
1900–1909, inclusive ...	4,219	5,485
1910–1919 „ ...	3,270	4,251
1920–1929 „ ...	2,899	2,899
1930–1939 „ ...	4,314	4,314

There is a striking similarity in the results for the Ballisodare Fishery (Fig. 6) and of the "summer" fish for the whole of Ireland, except that the minimum in the case of the Ballisodare Fishery appears to be almost a decade before that for the country as a whole.

RÉSUMÉ.

1. A description of the Ballisodare River and its watershed has been given, and it is pointed out that, with the exception of the upper parts of the Owenbeg River and its tributaries and a few small unimportant streams, the tributaries of the Ballisodare River run over limestone, and the waters thereof are highly alkaline (Fig. 1).

2. Three fish passes were erected in the years 1851 to 1855 to provide passages for salmon over the three most difficult obstructions in the river. Plans of the passes and maps showing their situation are given, Figs. 2 to 5, and photographs of the passes in Plate 7.

3. Prior to 1854 less than a score of salmon were taken in the pool below the Lower Falls at Ballisodare. After obtaining an Act of Parliament giving him authority to carry out improvements and alterations to the course of the river, Edward Joshua Cooper commenced some preliminary experiments with a view to stocking the Arrow River with salmon. These experiments were a failure. In December, 1851, three pairs of ripe salmon were transferred from the River Moy to the Owenbeg River, and at the same time a small quantity of fertilised ova was deposited in the same river. In 1853 salmon fry were numerous in the river above the falls at Collooney, and in the following year about 170 grilse were netted and placed above the Upper Falls at Ballisodare. By 1858 the river had become well stocked with salmon.

4. The records of the catches for most years in the period 1880 to 1939, inclusive, were available (see record), and taking ten-year periods there was a decrease in the average annual catch until the period 1910 to 1919, inclusive, and thereafter the catches have tended to increase (Fig. 6). The catches in

the Ballisodare Fishery showed fluctuations similar to the catches of summer salmon for Ireland as a whole.

ACKNOWLEDGMENTS.

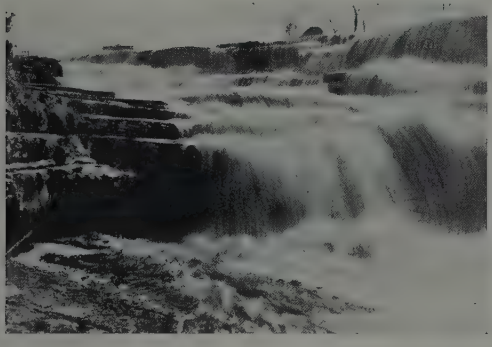
I should like to take this opportunity of expressing my thanks to Mr. G. P. Farran, B.A., Chief Inspector of Fisheries, Department of Agriculture, Fisheries Branch, Dublin, for the interest he has shown in this survey. My thanks are also due to Mr. Joseph Hanna, Assistant Librarian, Trinity College, Dublin, and Mr. E. Garette Gill, B.A., LL.B., for their help in the consultation of the necessary legal literature.

REFERENCES.

1. CALDERWOOD, W. L.—"Salmon Passes," Fisheries, Scotland, Salmon Fish, 1926. II.
2. Commissioners of Fisheries, Ireland, Report for 1854, Dublin, 31st October, 1855.
3. Commissioners of Fisheries, Ireland, Report for 1855, Dublin, 7th June, 1856.
4. Commissioners of Fisheries, Ireland, Report for 1856, Dublin, 31st May, 1857.
5. Commissioners of Fisheries, Ireland, Report for 1858, Dublin, 1st June, 1859.
6. FRANCIS, FRANCIS.—"Reports on Salmon Ladders," London, 1870.
7. HASSARD, A.—"Two Fish Passes on the River Shannon." Transactions of Institute of Civil Engineers in Ireland, Dublin. Vol. LXII. April, 1937.
8. Irish Law Reports, 1935.—Cooper *v.* Attorney-General and Others.
9. O'ROURKE, TERENCE.—"History, Antiquities and Present State of the Parishes of Ballysodare and Kilvarnet in the County of Sligo," Dublin, 1878.
10. SCHMIDT, CARL.—"Studier ofver Fiskvagar," Kungl. Landstruttsstyrelsen, No. 119 (No. 8, av 1906), Stockholm, 1906.
11. Statute I Vict., Cap. LXXXIX, 1837.—" An Act to enable Edward Joshua Cooper to establish and protect a salmon fishery upon the lakes and rivers of Owenmore and Arrow and also within the Bay of Ballisodare in the County of Sligo in Ireland."
12. Statute 5 & 6 Vict., Cap. 106.—"An Act to Regulate the Irish Fisheries" (10th August, 1842).
13. WENT, ARTHUR E. J.—"The Salmon Fishery." "A Statistical Survey of the Industry." Irish Trade Journal and Statistical Bulletin. Vol. XIII, Nos. 1 and 2. 1938.

a.

d.



b.

e.

c.

f.

PLATE 7.—PHOTOGRAPHS OF THE OBSTRUCTIONS AND FISH PASSES.

(a) Lower Falls, Ballisodare.
(b) East Bank, Lower Falls, Ballisodare.
(c) Lower part of the fish pass at the Lower Falls.
(d) Upper Falls, Ballisodare, showing the entrance to the fish pass.
(e) Fish pass at the Upper Falls, Ballisodare.
(f) Fish pass, Collooney, and part of the Falls.

A = Entrance of the fish pass.
B = Place where fish usually ascend the Upper Falls, Ballisodare.

No. 32.

SOIL AND FRESH-WATER IODINE-CONTENT IN IRELAND IN RELATION TO ENDEMIC GOITRE INCIDENCE.

By JAMES C. SHEE,
Chemistry Department, University College, Cork.

[Communicated by Professor J. Reilly.]

[Read June 18. Published separately August 30, 1940.]

A number of soil and water iodine analyses, carried out by the author in connection with his goitre survey in Ireland, are presented in this paper. This work represents an attempt to learn whether soil and water iodine-contents bear any relation to goitre incidence in Ireland. The preliminary survey has shown that among 9683 school-children under 14 years of age examined in Co. Tipperary S. Riding 27·67% were affected by goitre, the incidence ranging from as high as 60% around the Galtee Mountains and Slievenamon to as low as 6% in the northern part of the riding. In addition a survey of goitre among school-children in Galway City and surrounding rural area showed of 1318 children examined only one locally reared child to bear evidence of thyroid enlargement (1). Therefore a series of check analyses was carried out on samples from Galway. Some analyses were also carried out on samples from County Cork, although a school goitre survey was not made by me in that region.

Method.

The method of analysis employed was the Trevorrow and Fashena (2, 3) modification of Leipert's technique (4). Briefly this method consists of a chrom-sulphuric acid digestion of the substance to be analysed; this "wet-combustion" converts all iodine present into iodic acid. The digest is then heated to 180° C. to drive off acetic acid and other volatile substances formed in the process of the digestion. After cooling, a reducing agent is added to the digest; the flask is attached to a closed glass suction system, and the liberated iodine is distilled over into a KOH trap. Trevorrow and Fashena use phosphorous acid as the reducing agent, but in this investigation oxalic acid was used, as Baumann and Metzger (5) found it to give more satisfactory

returns with known quantities of iodine in both organic and inorganic combination. On completing the distillation, the iodine collected in the trap is estimated by Winkler's titrametric principle. The unit of iodine used in analyses is the microgram, or millionth part of a gram, represented by the Greek γ, and the results are expressed in terms of γ per kilogram, or γ per litre. Little difficulty was experienced in obtaining iodine-free reagents with the single exception of chromic acid. Several brands were tested against an iodine-free glucose solution until an iodine-free brand was found. A sufficient quantity of this was then bought to last through the series of experiments.

A theoretical contraindication to the use of oxalic acid as a reducing agent is the possible presence of dangerous amounts of CO in the effluent gas from the distilling apparatus (3). I have satisfied myself, however, that with the amount of oxalic acid used, i.e. 5 g., no appreciable quantity of CO comes over, as is shown by the absence of formation of Hb.CO in a dilute solution of hæmoglobin placed in train in the effluent.

With regard to the accuracy of the method in my hands, 20 samples of known amounts of KI of the order of 1 to 3 gamma mixed with glucose solution were estimated, with recoveries ranging from 86 % to 93 %, and averaging 89 %.

Water analyses.

Samples of 2,000 c.c. of water are taken for analysis and evaporated to small volume in a porcelain evaporation dish, to which 6 c.c. of 10 % KOH have previously been added, the residue is transferred with three washings to a 125 c.c. beaker, evaporated down to about 20 c.c., and transferred to a flask for digestion, for which 1 c.c. of chromic acid and 40 c.c. of sulphuric acid are sufficient.

For purpose of comparison with Irish results eight analyses were made of New York City tap-water. These show the consistency of the method, the results ranging between 1·35 and 1·50 gamma per litre, with a mean value 1·44. Hale (6) gives the closely approximating figure of 1·3 gamma/litre for the same water supply.

Three analyses of Cork City tap-water, at intervals of about a month, gave values of 3·1, 3·0, and 2·9 gamma/litre, or about twice the value of New York tap-water. (Results of the Irish experiments will be given to the first decimal place only, as the second decimal is beyond the control of the method.)

In Table 1 are given five values for the iodine-content of the river Suir, along about 40 miles of its course. The Suir is the main drainage river for the entire goitre area in Co. Tipperary. In the right-hand column is given the goitre percentage among school-children, for the immediate district whence the specimen was taken. There is a general tendency for the amount of iodine to diminish as the river proceeds on its course, but in each case the quantity of iodine is considerably greater than that for New York tap-water.

TABLE 1.

Iodine-content of the River Suir.

Source of Specimen.	Iodine γ per litre	% of goitre in neighbourhood.
Camus Bridge	4·7	8
Ballydrehid	3·3	60
Ardfinnan	3·9	43
Marlfield	2·3	12
Two Mile Bridge	2·1	31

Mean iodine-content = 3·3γ/litre.

Two samples of Corrib river water from the Galway district, where goitre is very rare, gave a mean value of 3·6γ/litre.

In Table 2 are given the iodine-contents of some village water supplies from South Tipperary. The pH of five of these waters is given also. There is clearly no correlation between the water pH and iodine-content in the samples tested, nor between water iodine-content and goitre incidence.

TABLE 2.

Iodine-contents of some village water supplies in South Tipperary.

Source of Specimen.	Iodine γ per litre.	pH of water.	% of goitre in neighbourhood.
Ballyporeen Pump	2·3	6·6	56
Skeehenarinky Pump ...	4·6	–	79
Ardfinnan Pump	4·7	–	43
R. Thonogue B'Looby ...	2·0	6·8	49
Clogheen Pump	1·6	6·4	66
Gormanstown Pump	2·3	7·2	28
Dundrum Pump	6·6	–	10
Knockavilla Pump	2·6	–	10
Aherlow River	2·4	7·6	23
Cashel Tap-water	2·3	–	19

Mean iodine-content = 3·1γ/litre.

Soil Iodines.

The acid "wet-combustion" method of iodimetry has been used before for water iodine analyses; but there is not, as far as I am aware, any account in the literature of its use in soil iodine analyses. All samples of soil were taken from pasture fields at a depth of about six inches, as iodine-content seems to vary with the depth of the soil (7). The soils were sampled on a glass or porcelain plate, pebbles and roots removed as far as possible, then dried for three hours in a water-oven, again sampled and debrided, rubbed down in a

mortar, and stored in glass-stoppered bottles. There is no loss of iodine in water-oven drying (8). Samples of one gram were analysed, and 1 c.c. of chromic acid and 40 c.c. of H_2SO_4 were usually found adequate to digest the organic matter in that quantity of soil. However, with soils containing a lot of humus such as peaty soils 2 c.c. of chromic acid and 50 c.c. H_2SO_4 were employed.

As this technique had not been utilised before for soil iodine analyses, numerous check and recovery experiments were run through before I decided that the method was reasonably accurate. I found that very thorough mixing and debridement of the soil were necessary, if accurate duplicates were to be obtained. Six consecutive pairs of observations on different soils whose iodine-contents ranged from 1850 to 5750 gamma per kilogram showed a maximum divergence of only 15 per cent. between the duplicate observations for any one soil. When it is remembered that samples of 1 g. were worked with, it will be seen that close approximations were obtained.

It was hardly expected that there would be found a direct relationship between the soil iodine of each individual specimen, on the one hand, and the absolute percentage of goitrous children living in the immediate neighbourhood whence that specimen was taken, on the other, as great variations both of goitre incidence and soil iodine values may be found in places only a mile or so apart; and in fact no such relationship could be shown.

The arbitrary figure of 15 % goitrous children among the primary school population represents roughly the point at which simple goitre ceases to be a harmless affliction of childhood, and tends to become a public health problem of some gravity.[1] In the upper two sections of Table 3 are contrasted the average soil iodine-contents of 12 districts in Tipperary with less than 15 % goitrous children, and 24 districts with more than 15 % goitre.

It can be seen that the average soil iodine-content in the under 15% goitre group is 5500γ/kilogram, and in the over 15 % goitre group it is only 3300γ/kilogram. A point of interest is the comparatively high values found for shell marl and for soil overlying outcropping coal measures. This is in accordance with the contention of Wilke-Dörfurt and Römersperger (9) that fossils generally, including coal, have a high iodine-content due to their organic origin.

[1] In the goitre-prophylaxis scheme recently inaugurated by Dr. M. Naughten, C.M.O.H. for Tipperary S.R., prevention is being practised in schools with 15 % and over of goitrous children.

TABLE 3.

Soil iodine-contents from various districts.

District.	Soil derived from	Iodine γ per kilogram of soil.
New Inn	Limestone	4700
Knockavilla ...	„	1900
Ardmayle	Alluvium	5900
Dundrum	Old Red Sandstone	2600
Marlfield	Shell Marl	10600
Mount Bruis ...	Limestone	6500
Shronell	„	3100
Emly	Old Red Sandstone	2600
Carrick on Suir ...	Alluvium	5800
Ballingarry ...	Coal Measures	7200
The Commons ...	„	11000
Ballincurry ...	„	5000
Tipperary. Less than 15% goitre.	Mean value =	5500
Ardfinnan	Limestone	3400
Ballylooby ...	„	1500
Gormanstown ...	„	3000
Ballydrehid ...	Alluvium	3300
Aherlow	Limestone	2300
Kilcash	Old Red Sandstone	1600
Clonmel	Limestone	2700
Ballyneale ...	„	4800
Ballyporeen ...	„	4700
Clogheen	Alluvium	4500
Kilsheelan	Limestone	1200
Castlegrace ...	„	5800
Grangemockler ...	„	3700
Poulacapple ...	„	700
Powerstown ...	„	3800
Newtownanner ...	Alluvium	2400
Killurney	Old Red Sandstone	1600
Ballagh	Limestone	1700
Bansha	„	3900
Tipperary Town ...	„	3400
Monard	Old Red Sandstone	3500
Kilvemnon ...	Limestone	5800
Ballydonnel ...	„	5600
Mullinahone ...	„	3700
Tipperary. More than 15% goitre.	Mean value =	3300
Spiddal	Granite	21,100
Furbo	„	83,200
Salerna	Peat	68,400
Barna	Granite	44,100
Newcastle	Felstone	21,000
R. Corrib Bank ...	Peat	32,000
Shantalla	Felstone	13,200
Western Galway.	Mean value =	40,400

Soil Iodines in Co. Galway.

Although a negative correlation has been clearly shown between soil iodine-content and goitre incidence in Co. Tipperary South Riding, it must be remembered that endemic goitre occurs throughout the whole region to a greater or lesser extent. Therefore it seemed desirable to run a series of analyses in a district in which endemic goitre does not occur, or is rare. As has been shown, Galway is such a district; and in the third section of Table 3 is set out the result of analyses of Co. Galway soils taken from the districts in which the school-children were clinically examined.

The mean content of these soils is 40,400γ/kilogram, which is ten times as great as the average value for all Tipperary soils examined (4,000γ/kilogram). These figures are of undoubtedly great significance when the extremely low incidence of goitre in the Galway district is compared with the 27·67% incidence for Co. Tipperary S.R. as a whole.

Eleven samples of soil from the neighbourhood of Cork City were analysed, and gave an average value of 8,500γ/kilogram. No goitre survey was made by me in this region, but to judge by the School Medical Officer's Reports, the incidence lies between the high Tipperary figures and the low Galway figures.

Table 4 gives a résumé of all the types of soil analysed, and it will be noticed that granite and peaty soils have far and away the highest iodine-content, while soils derived from alluvium, limestone, and old red sandstone show low values.

TABLE 4.

Iodine-contents for various types of soil.

Soils derived from	Number of localities.	Iodine γ per kilogram of soil.
Granite	3	49,500
Peat	4	46,300
Carboniferous Slate ...	3	17,700
Felstone	2	17,100
Marl	2	10,600
Coal Measures	3	7,700
Alluvium	8	4,400
Limestone	28	3,800
Old Red Sandstone	7	3,200

Discussion.

In this investigation no correlation could be shown between water iodine-content and goitre distribution in Ireland. Not very many specimens of water were assayed, as early results were sufficiently decisive to show that further investigation would likely prove to be unprofitable.

Thus two specimens from the river Corrib, draining a non-goitre region in Co. Galway, gave a mean value of 3·6γ/litre; while five specimens from the river Suir, whose catchment area corresponds almost exactly to the goitrous portion of Co. Tipperary, gave a mean value of 3·3γ/litre. Ten samples of village water supplies in Co. Tipperary S.R. (see Table 2) averaged 3·1γ/litre, and three tap-waters in Cork City, where goitre is probably much less frequent than in Co. Tipperary, averaged 3·0γ/litre. All these figures in turn are more than twice as high as the figure of 1·4γ/litre for New York City tap-water, where, whether we accept Olesen's (10) low or high figures of 3·0–15·9 % for girls, and 1·6–20·3% for boys, the occurrence of goitre is much less than in Tipperary S.R.

It may be pointed out here that the iodine-content of water does not necessarily reflect the iodine-content of the soil through which it flows. Usually a soil will contain at least a thousand times as much iodine by weight as the water flowing through it. Many factors, such as the texture, pH, chemical constitution, and presence of little or much organic matter in the soil, may influence the solubility of the soil iodine. Generally speaking, an acid soil tends to hold its iodine, and an alkaline soil to lose it by leaching.

The soil iodine analyses showed a definite negative correlation between goitre incidence and soil iodine-content. This negative correlation appeared not only between the regions of high and low goitre incidence in Co. Tipperary S.R., but to a marked degree between Co. Tipperary S.R. as a whole and the western part of Co. Galway, where goitre is almost non-existent.

In examining the cause of the low soil iodine-content of the portion of Co. Tipperary investigated, one is immediately struck by the fact that almost the whole area is overlain by a deep deposit of glacial drift, practically co-terminous with the goitre region. This drift usually occurs in the form of limestone gravel. It is a product of the last Ice Age, being laid down possibly as recently (geologically speaking) as twenty thousand years ago, and indicates that a very thorough leaching of the drift masses by melting ice has occurred. Iodine salts being very soluble would be washed away to the sea in large quantity.

The ice lingered longest on the mountains, which therefore received the most thorough leaching. To the present day the mountain regions in Tipperary have the least iodine-content and the most goitre. The leaching was facilitated by the fact that the glacial drift is largely limestone gravel, as limestone soils are porous and alkaline in reaction.

The high iodine-content of the Galway soils analysed is in part due to the proximity of the sea, and in part due to the chemical nature of the soils. McClendon concludes that the only iodine carried from the sea to the land is in the form of sea-spray blown by the wind, or in organisms fished from the sea. All the Galway soils were collected at a distance of at least a mile from the sea, and as far as possible on leeward slopes. Several soils in Co. Cork taken as near or nearer to the sea, and consisting of old red sandstone, limestone, or alluvial soils, did not show anything like so high an iodine-content.

The iodine-contents of the specimens from Furbo (83,200γ/kilogram) and

Salerna (68,400γ/kilogram) are noteworthy as being among the highest reported anywhere, and are in all probability due to the use of sea-weed as a soil fertiliser in these parts.

Plants are great concentrators of iodine, and, in addition, an acid soil favours enrichment (11), so that peaty soils which contain a good deal of humus, and are acid in reaction, should also be high in iodine. The four samples of peat soil analysed in my series show an average content of 46,300γ/kilogram. The lowest value of the four samples (16,100γ/kilogram) was in a specimen specially obtained in Tipperary, and showed the highest iodine-content of any specimen of Tipperary soil analysed.

Summary.

I. No correlation could be shown between fresh-water iodine-content and goitre incidence in Ireland.

II. A well-defined negative correlation was found to exist between soil iodine-content and goitre incidence.

III. The low soil iodine of the goitre district of Tipperary is explained by the nature of the soil, which is largely glacial drift in the form of limestone gravel that has undergone thorough leaching by the melting ice.

IV. The high soil iodine of the western part of Co. Galway, where goitre is rare, is partly due to the proximity of the sea, and partly to the igneous and peaty nature of the local soils.

This work was carried out during the tenure of a Fellowship from the Medical Research Council of Ireland.

My thanks are due to Prof. Reilly, who provided laboratory accommodation, and also to him and to Dr. P. J. Drumm for valuable criticism and advice on the conduct of the investigation.

REFERENCES.

(1) Shee (1939).—Irish Journ. Med. Sc., Sixth Series, No. 167, p. 802.
(2) Trevorrow and Fashena (1935).—Jour. Biol. Chem., **110**, 29.
(3) Fashena and Trevorrow (1936).—Jour. Biol. Chem., **114**, 351.
(4) Leipert (1933).—Biochem. Zeit., **261**, 436.
(5) Baumann and Metzger (1937).—Jour. Biol. Chem., **121**, 231.
(6) Hale, quoted by McClendon (1939).—"Iodine and the Incidence of Goitre." Univ. of Minnesota Press, p. 21.
(7) Mitchel, Warner, and Morrow (1928).—S. C. Agr. Sta., Clemson Agr. Coll., Bull. 252.
(8) Andrew (1930).—Analyst, **55**, 269.
(9) Wilke-Dörfurt and Römersperger (1930).—Z. anorg. allgem. Chem., **186**, 159.
(10) U.S. Pub. Health Repts., **41**, 2691 (1926); **44**, 1463 (1929).
(11) v. Fellenberg (1927).—Mitt. Lebensm. u. Hyg., **18**, 253.

SCIENTIFIC PROCEEDINGS.

VOLUME 22.

1.—Dissemination of Potato Viruses X and F by Leaf Contact. By J. B. LOUGHNANE and PAUL A. MURPHY, Albert Agricultural College, Glasnevin, Dublin. 1s. 6d. (May, 1938.)

2.—A Study of the Infiltration of Viruses into Seed Potato Stocks in the Field. By PHYLLIS CLINCH, J. B. LOUGHNANE, and PAUL A. MURPHY. 1s. 6d. (June, 1938.)

3.—Report of the Irish Radium Committee for the Year 1937. [Including Reports from The City of Dublin Skin and Cancer Hospital (*Radiologist*—DR. F. O. PILKINGTON); St. Anne's Hospital, Dublin (*Radiologist*—DR. OLIVER CHANCE); and by OLIVER CHANCE, M.B., B.CH., D.M.R.E., Richmond, Sir Patrick Dun's, Dr. Steevens', Rotunda, and Coombe Hospitals; and OSWALD J. MURPHY, M.B., B.CH., St. Vincent's Hospital, Dublin.] 1s. (July, 1938.)

4.—On a Recent Bog-flow in the County Wicklow. By G. F. MITCHELL. (Plate 1.) 1s. (July, 1938.)

5.—Subaqueous Transpiration. By H. H. DIXON, SC.D., F.R.S., Professor of Botany in the University of Dublin. 6d. (July, 1938.)

[Nos. 1 to 5, price 5s.]

6.—The Constitution of Laminarin. Isolation of 2 : 4 : 6-Trimethylglucopyranose. By VINCENT C. BARRY, M.SC., Chemical Laboratories, University College, Galway. 1s. (January, 1939.)

7.—A Study of the Seasonal Development of the Potato Plant in Relation to Blight Attack and Spraying. By PAUL A. MURPHY, Albert Agricultural College, Glasnevin, Dublin. 1s. (February, 1939.)

8.—Atmospheric Pollution in Dublin during the Year 1938. By A. G. G. LEONARD and BRIDGET P. MCVERRY, Chemical Department, University College, Dublin. 1s. (April, 1939.)

9.—The Ovule, Gametophytes, and Proembryo in *Saxegothaea*. By W. J. LOOBY and J. DOYLE (Botany Department, University College, Dublin). (Plates 2 and 3.) 3s. (May, 1939.)

10.—An Apparent Connection between the Presence of Colloids and the Osmotic Pressures of Conifer Leaves. By O. ROBERTS, M.SC., and S. A. STYLES, M.SC. 6d. (May, 1939.)

11.—Embryogeny in *Saxegothaea* and its Relation to other Podocarps. By J. DOYLE and W. J. LOOBY (Botany Department, University College, Dublin). 2s. (May, 1939.)

12.—"Studies in Peat." Part 5. Extraction of Peat with Azeotrope-like Petroleum mixed Solvents. By J. REILLY, D. F. KELLY, and J. DUFFY. 6d. (May, 1939.)

13.—Studies on the Ultimate Composition of Biological Material. Part III.—Glandular Tissues. By ROBERT PRESS and WILLIAM ROBERT FEARON. 6d. (May, 1939.)

14.—Report of the Irish Radium Committee for the Year 1938. Including Reports from OSWALD J. MURPHY, M.B., B.CH., St. Vincent's Hospital, Dublin; OLIVER CHANCE, M.B., B.CH., D.M.R.E., Richmond, Sir Patrick Dun's, Dr. Steevens', Rotunda, and Coombe Hospitals; and by St. Anne's Hospital, Dublin (*Radiologist*—DR. OLIVER CHANCE). 1s. (May, 1939.)

[Nos. 6 to 14, price, 10s.]

15.—Leaf Movement on Release of Sap Tension. By HENRY H. DIXON, SC.D., F.R.S., University Professor of Botany, Trinity College, Dublin, and J. S. BARLEE, B.SC., Assistant to the Professor of Botany, Trinity College, Dublin. (Plate 4.) 1s. 6d. (July, 1939.)

16.—"Studies in Peat." Part 6. The "Water Phase" in Azeotropic Extraction Solvents. By J. REILLY and D. F. KELLY. 6d. (July, 1939.)

17.—"Studies in Peat." Part 7. Water Distribution in Peat Wax Azeotropic Extraction Solvents. By J. REILLY, D. F. KELLY, J. DUFFY, and E. COUGHLAN. 6d. (July, 1939.)

[Nos. 15 to 17, price 2s.]

18.—On a Recent Bog-flow in Powerscourt Mountain Townland, Co. Wicklow. By A. D. DELAP and G. F. MITCHELL. 6d. (December, 1939.)

19.—The Chemical Constituents of Lichens found in Ireland. *Lecanora Gangaleoides*—Part 2. By T. J. NOLAN, B.A., D.SC., and J. KEANE, PH.D., University College, Dublin. 1s. (February, 1940.)

20.—Further Experiments on Transpiration into a Saturated Atmosphere. By HENRY H. DIXON, SC.D., F.R.S., Professor of Botany in Trinity College, Dublin, and J. S. BARLEE, B.SC., Lecturer in Biology, Royal Naval College, Dartmouth. (Plate 5.) 1s. 6d. (February, 1940.)

21.—Stabilised Diazo Complexes with Piperazine and other Bases. By P. J. DRUMM, W. F. O'CONNOR, and J. REILLY, Chemical Dept., University College, Cork. 6d. (March, 1940.)

22.—The Requirements of the Pig for Vitamins A and D. By BRENDAN J. SENIOR, M.SC., Animal Nutrition Department, University College, Dublin. (Plate 6.) 1s. (April, 1940.)

23.—The Chemical Constituents of the Lichen *Parmelia Latissima* Fée. By T. J. NOLAN, B.A., D.SC., J. KEANE, PH.D., and V. E. DAVIDSON, B.SC., University College, Dublin. 6d. (April, 1940.)

24.—New Observations on the Life-history of *Callitris*. By W. J. LOOBY and J. DOYLE, University College, Dublin. 1s. 6d. (May, 1940.)

[Nos. 18 to 24, price 6s.]

25.—Atmospheric Pollution in Dublin during the Year 1939. By A. G. G. LEONARD, BRIDGET P. MCVERRY, and D. CROWLEY. 1s. (May, 1940.)

26.—Studies in Peat. Part 8. Preliminary Note on Irish Peat Wax (Mona Wax). By J. REILLY and J. A. EMLYN. 6d. (May, 1940.)

27.—Report of the Irish Radium Committee for the Year 1939. Including Reports from OSWALD J. MURPHY, M.B., B.CH., St. Vincent's Hospital, Dublin; OLIVER CHANCE, M.B., B.CH., D.M.R.E., Richmond, Sir Patrick Dun's, Dr. Steevens', Rotunda, and Coombe Hospitals; DR. R. E. TOTTENHAM, City and County Hospital, Londonderry; St. Anne's Hospital, Dublin (*Radiologist*—DR. OLIVER CHANCE). 6d. (June, 1940.)

28.—The Production of Santonin from Irish-Grown Artemesia. By PETER J. DRUMM, PH.D., D.SC., and WILLIAM F. O'CONNOR, M.SC. 6d. (June, 1940.)

29.—A Molecular Constant for Soured Milks. II. Effect of Preservatives. By J. J. RYAN and G. T. PYNE (Department of Dairy Chemistry, University College, Cork). 6d. (June, 1940.)

30.—Award of the Boyle Medal to Professor Joseph Reilly.

31.—Salmon of the Ballisodare River. I.—History of the Ballisodare Fishery. By ARTHUR E. J. WENT, Department of Agriculture, Fisheries Branch, Dublin. (Plate No. 7.) 2s. 6d. (August, 1940.)

32.—Soils and Fresh-water Iodine-Content in Ireland in Relation to Endemic Goitre Incidence. By JAMES C. SHEE, Chemistry Department, University College, Cork. [Communicated by Professor J. Reilly.] 1s. (August, 1940.)

[Nos. 25 to 32, price 6s.]

PRINTED BY FONSONBY AND GIBBS, UNIVERSITY PRESS, DUBLIN.